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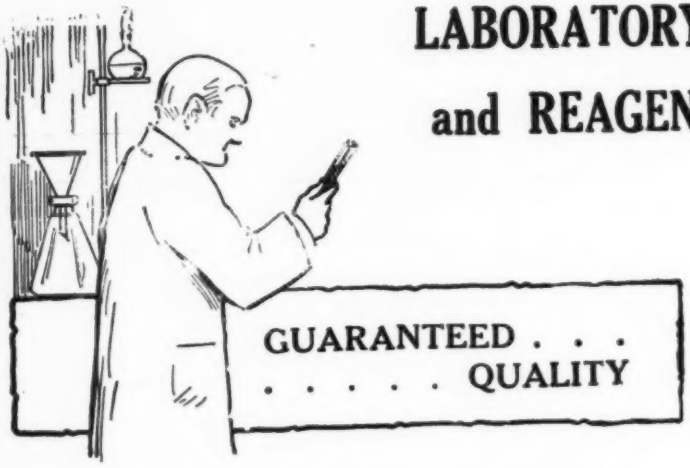

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[Jour. Indian Chem. Soc., Vol. 30, No. 2, 1953]

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RECENT ADVANCES IN THE CHEMISTRY OF SESQUITERPENES*

By Dr. P. C. Guha, D.Sc., F.N.I.

Prior to the introduction of dehydrogenation as a tool in establishing the carbon framework of various alicyclic compounds, the structures of just a few sesquiterpenes had been known with any certainty. Ruzicka and his collaborators[1] are mainly responsible for the successful application of this method in settling the nuclear structure of various sesquiterpenes. Though active interest has been displayed in the field after that, the present decade has been especially fruitful, and at present the structures of several compounds are definitely established, and in some cases the finer details of the constitution have also been worked out. This report will cover the progress made during the period 1943-1952.

A careful perusal of the research work carried out over last several decades will reveal that the older methods of structure-determination have not been very successful either because the degradation products are too complex to admit of separation and identification or are too simple to throw any light on the original molecule. The most profitable researches centre round the newer methods of organic chemistry. *Dehydrogenation* has proved to be extremely useful in settling the structures of various sesquiterpenes, especially the bicyclic hydrocarbons and their derivatives. At present, on its basis, four well known groups are recognised, viz., cadalene, eudalene, guaiazulene and vetivazulene. Some compounds give rise to any one of these products as a result of simple dehydrogenation of the original bicyclic structure, while others may yield the same substance by dehydrogenation when either a ring-closure or a ring-fission has also occurred. Usually it is quite easy to differentiate if besides dehydrogenation any other reaction has also taken place. A very useful extension of the dehydrogenation method involves the technique of labelling a double bond with an additional methyl group, a process easily carried out by the interaction of the hydrocarbon epoxide with methylmagnesium iodide, followed by dehydration and dehydrogenation. This method was first employed by Ruzicka and Sternbach[2] in locating the nuclear double bond of *dextro*-pimaric acid. The process has been used with advantage in the case of cadinene[3] *iso*zingiberene[4], copaene[5] and a cadinenic sesquiterpene from the oil of *Hardwickia pinnata*[6]. All the the theoretically possible methylcadalenes[7] have been synthesised in this laboratory. In the eudalene series, most of the required naphthalene derivatives were synthesised in connection with the location of the carbonyl group of tetrahydrocyperone[8]. Much more synthetic work will have to be carried out in the azulene series in order to get the alkyl derivatives of guaiazulene and vetivazulene which will ultimately serve as reference substances.

*Presidential Address at 29th Annual General Meeting of the Society, held on January 3, 1953, at Lucknow.

Reduction carried out by sodium in liquid ammonia has also proved useful. Two aspects of this reduction procedure have given quite fruitful results on the synthetic side. Synthesis of β-curcumene[9] makes use of this procedure for converting an aromatic system, easily accessible by usual synthetic methods, into the required dihydro derivative, which is otherwise difficult to synthesise. Reduction of a methyl ether of a phenol by this method, followed by a mild hydrolysis leads to quite useful unsaturated ketones, which may serve as intermediates in the synthesis of naturally occurring substances. (±)-γ-Curcumene[9] and (±)-zingiberene[10] have recently been synthesised by this method. Another unusual application of this method will be found under the section on lanceol (p. 84).

Selenium dioxide and *NBS* may be expected to play a useful role in the field of sesquiterpenes. An important application has been described under β-caryophyllene (p. 88).

The various physical methods have proved quite useful in the terpene field in general. The use of *molecular refractivity* is too well known. Sutherland[14] has further extended the scope of this property by his method of graphical representation.

Ultraviolet spectra have proved very useful in locating two or more carbon—carbon or carbon—oxygen double bonds in conjugation. With the help of Woodward's rules[12] and the exact positions and intensities of the bands, it is possible to get useful information about the degree of substitution in such a system. Several examples will be found in the text. In the azulene series, visible and to some extent the ultraviolet spectra are of great assistance in locating the positions of the nuclear alkyl groups[13].

In recent times *infra-red spectra* are playing an ever increasing and useful role in organic chemistry in general. The method has two main uses: for the characterisation of the molecule as such, and for the identification of various atomic groupings in a particular compound[14]. Sorm and his co-workers[15] have developed a new technique for determining the fundamental type of the sesquiterpenes and their derivatives. The method depends on taking the infra-red spectra of the fully saturated and de-oxygenated hydrocarbon and comparing it with those of the well known types, e.g. perhydrocadinene, perhydrohumulene, etc. Though stereoisomerism was supposed to introduce some complications, the method has been found to be quite useful.

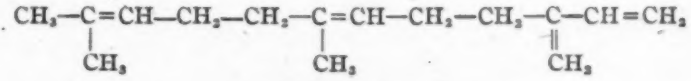
In structure-determination, infra-red spectra can at once indicate the presence or otherwise of various atomic groupings. In detection of ethylenic linkages it has the further advantage of giving some information about the degree of substitution on the double bond[16]. For determining the size of an alicyclic ring it is just necessary to determine the carbonyl frequency of that system. Useful application of these procedures will be found under the various sesquiterpenes, e.g. caryophyllene, chigadmarene, etc.

Another great advance in recent times relates to the introduction of *efficient fractionating columns and chromatography* for the isolation of pure substances, as it is of fundamental importance to deal with purest possible samples for the determination of structure. Previous methods, in general, failed to yield analytically pure samples, as the terpenes usually occur as mixtures of closely related substances.

For the present address, the acyclic sesquiterpenes and their derivatives will be taken up first, followed by the monocyclic, bicyclic and tricyclic groups.

Acyclic

Farnesene.—The acyclic group of sesquiterpenes, as at present constituted, is a small one and till 1949 only two members, viz., farnesol and nerolidol, were known. Sorm and co-workers[17] isolated an aliphatic sesquiterpene with four double bonds from the essential oil of hops and this constitutes a small percentage of the sesquiterpene fraction. Its separation was effected by repeated chromatography over Al_2O_3. The earlier workers, who did not have these finer methods of ioslation at their disposal, had missed it in the essential oil. On the basis of ozonisation and spectral measurements the compound has been shown to be (I).



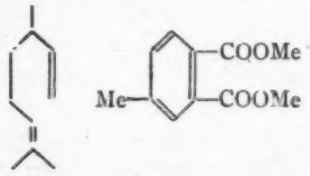
(I) Farnesene.

This is identical with β-farnesene, which can be obtained mixed with α-farnesene by the dehydration of farnesol with potassium hydrogen sulphate[18].

Monocyclic

The reaction of methylacetylene dicarboxylate with zingiberene has recently been investigated[19]. The adduct on pyrolysis yielded a hydrocarbon $C_{10}H_{16}$, identified by its infra-red spectrum as (II), together with dimethyl 4-methylphthalate (III). These results are inconsistent with the earlier structure proposed by Ruzicka and van Veen[20] and consequently it has been overthrown in favour of (IV). (±)-Zingiberene has been synthesised by Mukherji and Bhattacharya[10,21].

When zingiberene is treated with Bertram-Walbaum reagent, a bicyclic hydrocarbon, termed *iso*zingiberene, is produced. This gives cadalene on dehydrogenation and the position of the two double bonds in the molecule has been established by Soffer, Steinhardt, Turner and Stebbins[4] by employing the labelling technique of Ruzicka and Sternbach, a method which has been briefly outlined in the introduction. *iso*Zingiberene is now represented by (V).



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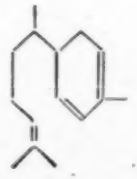

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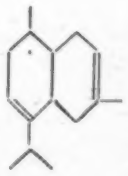
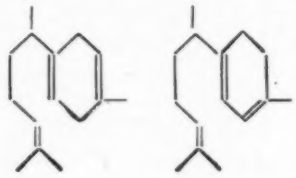


(V)

Curcumenes.—1-β-Curcumene (VI) occurs in the essential oil from the rhizomes of *Curcuma aromatica*, Salisb. The structure which had been arrived at by Carter, Copp,

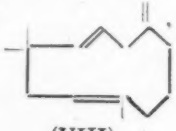
Rao, Simonsen and Subramaniam[23] as a result of degradative studies, has now been confirmed by its synthesis in the (±)– form by Birch and Mukherji[9]. Batt and Slater[28] have recently described the isolation and examination of another closely related sesquiterpene, viz. γ-curcumene (VII). Its synthesis has also been achieved by Birch and Mukherji[9].



(VI) (VII)

These syntheses have been made possible only by the introduction of a new reduction procedure, the scope of which has been briefly discussed earlier.

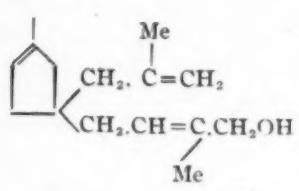
Humulene.—Humulene, the chief sesquiterpene of the essential oil of hops (from *Humulus lupulus*, L.) has recently been the subject of a number of investigations. Sorm and his collaborators[17,24] have definitely proved the identity of "α-caryophyllene" with this hydrocarbon, and since it has been shown to be a monocyclic hydrocarbon with no apparent close relationship with β-caryophyllene, the term "α-caryophyllene" should be dropped in preference to humulene. These authors also were the first to show that humulene was a monocyclic hydrocarbon with three ethylenic linkages; they further investigated the hydrogenation and ozonolysis of the compound and prepared a crystalline trioxide, m.p. 122.5° (cf. Ref. 25). Humulene on treatment with Aschan's reagent yields a crystalline, fully saturated tricyclic alcohol, m.p. 116° which appears to be identical with the α-caryophyllene alcohol of Asahina and Tsukamoto[26]. Recently, very interesting degradation studies have been carried out by Clemo and Harris[27]. Interesting suggestion[26,27] has been made that humulene may be represented by (VIII) which represents it as a derivative of *cyclo*undecane. Much further work remains yet to be done to finally settle the question of its constitution.



(VIII)

Lanceol.—Lanceol is a primary monocyclic sesquiterpene alcohol, present in the essential oil from the wood of *Santalum lanceolatum*. Bradfield, Francis, Penfold and Simonsen[28], who carried out the initial investigations, represented it provisionally by (IX). On the basis of U. V. spectral measurements and synthetic work, Owen[29] deduced evidence which definitely disproved the provisional structure. Recent work by Birch and Murray[30] has finally solved this problem. They showed that from the published evidence lanceol may most probably be represented by (X), the $C_{11}H_{14}O_5$ acid obtained on its ozonolysis being best represented by (XI), which must have resulted by a ring-closure of the primary product of ozonolysis, which must be (XII). The

structure (XI) explains all of its properties and on further ozonisation this acid smoothly gives the known acid (XIII). Finally, the structure (XI) has been confirmed by a synthesis.



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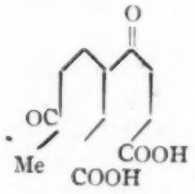

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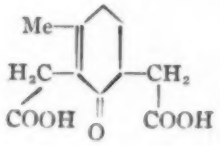

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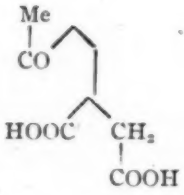

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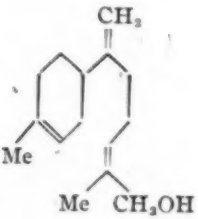

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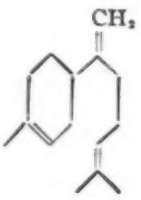


(XIV)

A crucial proof of the correctness of this structure has been afforded by the hydrogenolysis of lanceol to β-biasabolene (XIV), with sodium and ethanol in liquor ammonia.

Bicyclic

This is an important class of sesquiterpenes and the various hexahydro derivatives of cadalene, eudalene, guaiazulene and vetivazulene fall under this sub-group. Ruzicka, Schinz and Muller[31] have described the isolation of another new type of bicyclic sesquiterpene from the essential oil of the leaves of *Cedrus atlantica*, Manetti. This hydrocarbon on dehydrogenation furnished a novel naphthalene derivative, $C_{15}H_{18}$, which has not as yet been characterised, though it does not appear to contain an *iso*propyl group. Recent work at Bangalore[32] has shown the presence of another similar type of hydrocarbon in the essential oil from the wood of Himalayan cedar; the new sesquiterpene, α-himachalene appears to be closely related to the hydrocarbon of Ruzicka, Schinz and Muller, but is definitely different from it. Another isomer, β-himachalene, and a tertiary alcohol, himachalol, are also present and yield the same dihydrochloride as is obtained from α-himachalene.

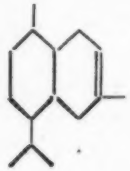
Carotol has been depicted as a derivative of 1:7-dimethyl-4-*iso*propylnaphthalene and is a unique specimen in itself. Its chemistry will be shortly discussed.

Besides these types which can be regarded as derivatives of naphthalene and azulenes, various other members represent different bicyclic systems. Important examples are β-caryophyllene and β-santalol.

Cadinene.—Cadinene is one of the most widely distributed sesquiterpenes[33]; however, it is likely that many "cadinenes" may be only structural isomers, differing in position of the double bonds about C_1 and C_6.

Cadinene, as regenerated from its dihydrochloride, has recently been shown by Campbell and Soffer[3] to possess the structure (XV).

Though the basic structure of cadinene was demonstrated by its dehydrogenation to cadalene by Ruzicka and Meyer[34] several decades ago, the location of the double bonds had remained uncertain. Cadinene dioxide (XVI) on interaction with methyl-magnesium iodide, followed by dehydration and dehydrogenation with selenium yielded 1 : 2 : 6 : 7-tetramethyl-4-*iso*propylnaphthalene (XVII), identified by a synthesis. This, thus, fixes the position of the ethylenic linkages in cadinene between C_1-C_2 and C_6-C_7 as in (XV).



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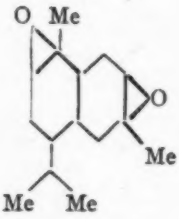

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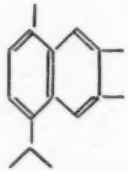
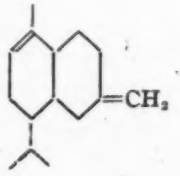


(XVII)

Cadinene on treatment with Bertram-Walbaum mixture, or with formic acid at 100°, etc. yields an isomerised product termed *iso*cadinene. Gillam, Moss and West[35] have recently shown it to be non-homogeneous, and hence, not a chemical individual as regarded earlier by Robertson and Henderson[36].

A *dextro*-rotatory cadinenic sesquiterpene has been isolated from the essential oil of *Hardwickia pinnata*[6] and shown to be a structural rather than a stereoisomer of *l*-cadinene. On the basis of ozonolysis and dehydrogenation experiments it has been shown to be a mixture of (XVIII) and (XIX); the two isomers could not be separated by fractional distillation.



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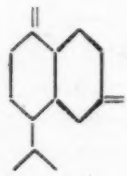
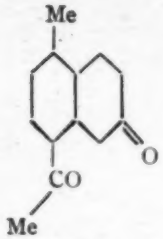


(XIX)

Sesquibenihene.—The essential oil from *Chamaecyparis formosensis* has been shown by Katsura[37] to contain a bicyclic sesquiterpene of the cadalene group. Sesquibenihene, as it has been called, gave formaldehyde on ozonolysis, along with a diketone $C_{13}H_{20}O_2$ (XX) which on oxidation with cold sodium hypobromite solution gave an acid $C_{12}H_{18}O_2$ which must be represented by (XXI), as on dehydrogenation it furnished 1-methylnaphthalene. On the basis of these experiments sesquibenihene has been represented by (XXII).



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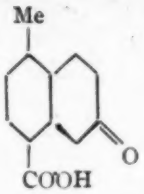

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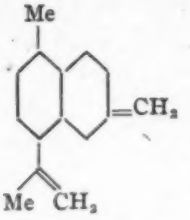
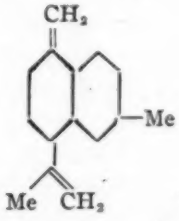


(XXII)

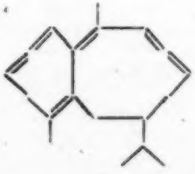
Another sesquiterpene, isolated from the essential oil of the leaves of guava (*Pesidium guayva*) and shown to give cadalene on dehydrogenation, has been provisionally represented by (XXIII) on the basis of its reactions[28].



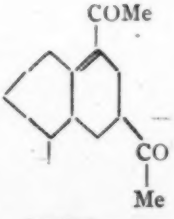
(XXIII)

Chigadmarene.—From the essential oil of *Lansium annamalayanum*, Rao, Dutt, Sukh Dev and Guha[29] isolated a new bycyclic hydrocarbon, which was shown to belong to the *s*-guaiazulene (XXIV) family. The presence of two ethylenic linkages in the molecule was confirmed by perbenzoic acid titration and quantitative hydrogenation. On the basis of infra-red spectrum it could be deduced that linkages of the type $R_1HC=CR_2R_3$ were absent and an exocyclic double bond was probably present[49].

Ozonolysis gave only formaldehyde and a ketone $C_{14}H_{20}O_2$ which has possibly arisen as a result of the ring-closure of the primary product of ozonolysis, $C_{14}H_{22}O_3$. As a result of the various reactions of this diketone, it has been represented by (XXV) and consequently α-chigadmarene by (XXVI).



(XXIV)



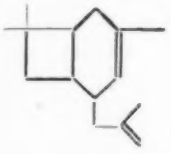
(XXV)

(XXVI)

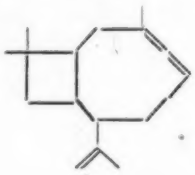
β-Caryophyllene.—β-Caryophyllene is probably the most widey distributed sesquiterpene occurring in nature[41]. It occurs to a considerable extent in the essential oils of *Hardwickia pinnata*[42] and *Dipterocarpus indicus*[43]. Very often it occurs along with humulene.

β-Caryophyllene is one of the most widely investigated hydrocarbons, but notwithstanding the number of well known chemists who attacked the problem, the terpene evaded all attempts at structure elucidation till very recently. Dehydrogenation could not give any clue about its carbon framework. The degradation studies[44] began in 1908 or so, culminated in 1951 in the establishment of its structure, which is unique in the sense that this is the first known derivative of *cyclo*nonane occurring in nature.

New trends in the investigation of this sesquiterpene began with the publication of a paper by Treibs[45] on the oxidation of β-caryophyllene with hydrogen peroxide in the presence of vanadium pentoxide to the crystalline epoxide. This can also be prepared by the action of perbenzoic acid or on auto-oxidation. The oxide has been shown to occur in French lavender oil[46] and also in the benzene extract of cloves[47] which is found to be devoid of caryophyllene. Apparently the caryophyllene is formed from this precursor during steam distillation. The caryophyllene-oxide, $C_{15}H_{24}O$, on oxidation with permanganate in acetone solution yielded two isomeric oxido-glycols $C_{15}H_{26}O_3$ and an oxido-ketone $C_{14}H_{22}O_2$, m.p. 61-62°. This oxido-ketone, unexpectedly, did not give the bromoform reaction, a fact which could not be explained on the basis of earlier structures (XXVII, Ruzicka[48]) and (XXVIII, Rydon[49]) and consequently Treibs proposed the alternative formula (XXIX). There were three more structures proposed depending on the structure of caryophyllenic acid as (XXX) or (XXXI).

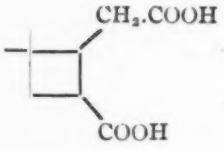


(XXVII)

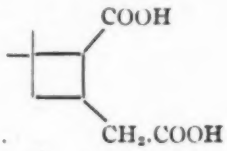


(XXVIII)

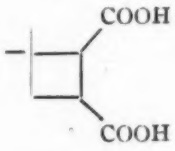
(XXIX)



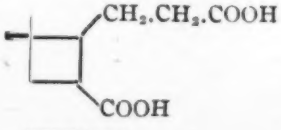
(XXX)



(XXXI)



(XXXII)



(XXXIII)

The presence of a *cyclo*butane ring carrying a *gem*-dimethyl grouping had been fully established in 1936 when (±)-*trans-nor*caryophyllenic acid (XXXII) was synthesised[50]. A decision about the structure of caryophyllenic acid had yet to be arrived at. Barton[51] in 1950 pointed out that the known reactions of caryophyllenic acid can be well explained only by the structure (XXX). Confirmation of this view came from three independent sources. Dawson and Ramage[52] synthesised the alternative acid (XXXI) and found it to be different from caryophyllenic acid. An interesting series of reactions by Eschenmoser and Furst[53] leading eventually to 4 : 4-dimethyl*cyclo*hexanone, also gave evidence in favour of (XXX), and finally Campbell and Rydon[54] carried out a straightforward synthesis of the acid (XXX) and proved it to be identical with caryophyllenic acid by comparison of the infra-red spectra.

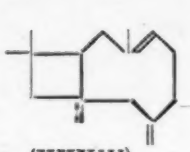
One of the principal and most characteristic degradation products of β-caryophyllene is the keto-acid $C_{11}H_{18}O_3$ which on hypobromite oxidation gives homocaryophyllenic acid, which has been proved on the basis of synthetic experiments to be (XXXIII)[55].

Sorm, Dolejs and Pliva[56] examined infra-red spectrum of the oxido-ketone $C_{14}H_{22}O_2$ of Teirbs, referred to above, and by a comparison of the carbonyl frequency (1693 cm^{-1}) with the values known for the *cyclo*hexanones, *cyclo*heptanones, etc., concluded that the carbonyl group in $C_{14}H_{22}O_2$ probably formed a part of a nine-membered ring. Moreover, dihydro-β-caryophyllene oxide by oxidation with loss of two ring-carbon atoms and cyclisation of the resulting dicarboxylic acid gave a ketone $C_{12}H_{20}O_2$ with a band at 1705 cm^{-1}. This clearly showed the presence of a *cyclo*heptanone ring in the new ketone and consequently the presence of a *cyclo*nonane ring in the oxido-ketone was placed on a firm basis. Bearing on this evidence, they suggested a structure of type (XXXIV) for β-caryophyllene.

In an important paper, Barton and Lindsey[57] adduced chemical evidence in favour of the formula (XXXIV). However, further work[55,58] based on oxidation of the crystalline nitro-nitrosite with permanganate, and especially the structure of homocaryophyllenic acid, showed that β-caryophyllene is best represented by (XXXV). In terms of this structure, some of the important reactions of β-caryophyllene shall be illustrated.

The oxido-ketone of Treibs now must be represented by (XXXVI). This, when refluxed with methanolic potassium hydroxide, gave a highly crystalline, saturated (hence tricyclic) keto-alcohol (XXXVII) which on further oxidation gave an almost quantitative yield of a saturated diketone (XXXVIII). Since this on selenium dioxide oxidation gave the compound (XXXIX), proved on spectroscopic data to contain the chromophone —CO-C=C-CO-, the occurrence of the oxygen atoms in (XXXVIII) and consequently in (XXXVII) as 1 : 4 to each other was placed on a sound evidence. This unsaturated diketone $C_{14}H_{18}O_2$ on oxidation with $KMnO_4$ in acetone solution or with nitric acid gave a saturated bicyclic dicarboxylic acid $C_{12}H_{18}O_4$, which can be represented by (XL)[57]. The various properties of this acid, e. g. its

facile conversion into an anhydride, resistance to alkaline hydrolysis of its dimethyl ester etc. could easily be explained on the basis of this structure [59–61].



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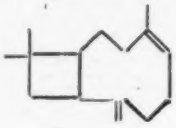

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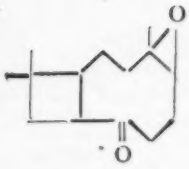
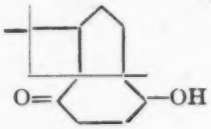
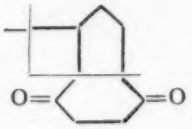


(XXXVI)



(XXXVII)

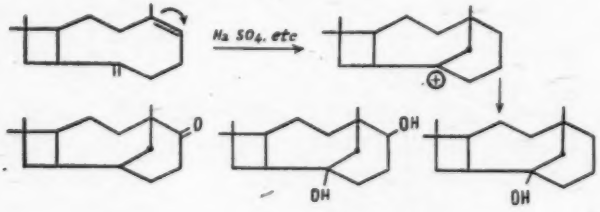


(XXXVIII)

(XXXIX)

(XL)

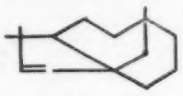
β-Caryophyllene is known to isomerise readily to tricyclic compounds. It is readily isomerised, for example, by Bertram-Walbaum mixture, or Aschan's reagent or hot formic acid to a saturated tricyclic, crystalline alcohol. On the basis of caryophyllene as (XXXV), this transformation can be readily visualised as taking place as follows; β-caryophyllene alcohol then becomes (XLI). Similarly, the glycol,



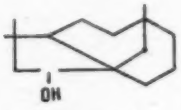
(XLIII) (XLII) (XLI)

$C_{15}H_{26}O_2$ formed as a by-product in the hydrogen peroxide oxidation of β-caryophyllene[45], can be regarded as (XLII), formed by an electrophylic attack by OH^+. This glycol on CrO_3 oxidation yielded a crystalline monohydroxy-ketone (XLIII) which was resistant to further oxidation. Wolff-Kishner reduction of this hydroxy-ketone furnished β-caryophyllene alcohol (XLI).

Reasoning similarly, α-caryophyllene alcohol and clovene have been formulated as (XLIV) and (XLV) respectively[59].



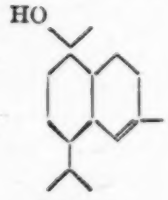
(XLV)



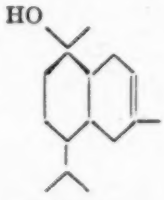
(XLIV)

The formula of clovene is supported by its infra-red spectrum[62].

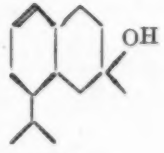
Cadinol.—The term "cadinol" has in general been applied to a *tert.*-sesquiterpene alcohol containing two rings which on treatment with gaseous hydrochloric acid gives cadinene dihydrochloride. Cadinols have been isolated from a number of essential oils[63]. In view of the new structure for cadinene dihydrochloride, α-, β- and γ-cadinols, for example, may be represented by (XLVI), (XLVII) and (XLVIII) respectively.



(XLVI)



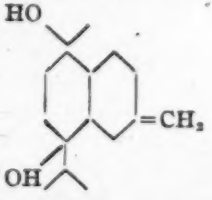
(XLVII)



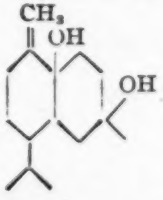
(XLVIII)

Calamendiol.—Calamendiol, $C_{15}H_{26}O_2$, is a crystalline bicyclic sesquiterpene ditertiary alcohol containing one ethylenic linkage, and has been isolated from the essential oil of *Acorus Calamus*[64].

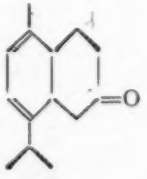
It has been recently investigated by Treibs[65]. On dehydrogenation it gives cadalene, and ozonolysis yields a crystalline dihydroxyketone, $C_{14}H_{24}O_3$, which does not contain the grouping $-COCH_3$. Dehydration afforded the unsaturated ketone, $C_{14}H_{20}O$, which showed little tendency to isomerise to a phenol. Based on these and similar considerations Treibs has represented calamendiol by (XLIX) when the doubly unsaturated ketone, $C_{14}H_{20}O$, becomes (L). Simonsen[64] has pointed out that the structure (LI) explains the above reactions equally well and in fact (LII) explains the failure of the ketone to isomerise to a phenol in a better way.



(XLIX)



(LI)



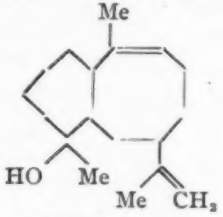
(L)

(LII)

A distinction between the structures (L) and (LII) and consequently between (XLIV) and (LI) can be readily made on the basis of ultraviolet spectrum of the ketone[66].

Partheniol.—It is a bycyclic sesquiterpene alcohol $C_{15}H_{24}O$, m. p. 127-28° of the *s*-guaiazulene family. Its structure has been elucidated by Haagen-Smit and Fong[67]. It occurs as the cinnamate in guayule (*Parthenium argentatum*, Gray).

The tertiary nature of the alcoholic group was readily revealed by its indifference to esterification and ease of dehydration. Dehydrogenation with sulphur yielded *s*-guaiazulene, and hence it remained only to fix the positions of the two double bonds and one tertiary hydroxyl. This was settled by a study of the products of ozonolysis of partheniol and anhydro-tetrahydroparentheniol and the application of Blanc's rule to the suitably constituted dicarboxylic acid obtained by stepwise degradation. The structure (LIII) for partheniol, is thus well established.

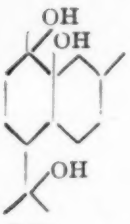


(LIII)

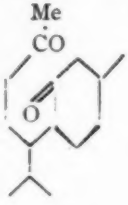
Carotol.—Carotol, $C_{15}H_{26}O$, occurs in the essential oil of *Daucus carota* L. and it has recently been investigated by Sorm and Urbanek[68] who have assigned to it the structure (LIV). That it is a derivative of 1:7-dimethyl-4-*iso*propylnaphthalene has been established by dehydrogenation over palladised charcoal.

$KMnO_4$ oxidation afforded a crystalline triol (LV) which on cleavage with lead tetra-acetate gave a diketone $C_{13}H_{20}O_3$, m. p. 98° (LVI), containing the $-COCH_3$ grouping. Dehydration of dihydrocarotol, and its ozonolysis and CrO_3 oxidation gave results in support of (LIV).

(LIV)



(LV)

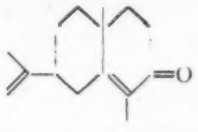


(LVI)

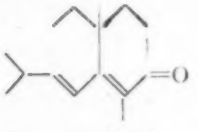
β-Cyperone.—α-Cyperone, a sesquiterpene ketone, $C_{15}H_{22}O$, of the eudalene series occurs in the essential oil from the tubers of *Cyperus rotundus*[69], and has been shown to possess the structure (LVII)[70]. On treatment with acid or alkali α-cyperone undergoes a rearrangement to yield another isomeric ketone, *β*-cyperone, with a higher molecular refractivity and optical rotation. *β*-Cyperone had been regarded as a stereoisomer of α-cyperone, differing in the disposition of the angular methyl and *iso*propenyl groups.

McQuillin[71] recently carried out a comparison of the ultraviolet spectra of their derivatives like the oxime, semicarbazone and 2:4-dinitrophenylhydrazone and

concluded that the two ketones were structural isomers rather than stereoisomers assigning (LVIII) as the most probable structure of β-cyperone.



(LVII)



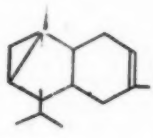
(LVIII)

TRICYCLIC

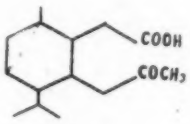
This represents an interesting class of sesquiterpenes and their derivatives. Though a somewhat difficult tract, because of the failure of the dehydrogenation procedure in many cases, yet α-santalol, a tricyclic primary sesquiterpene alcohol, was one of the earliest sesquiterpene derivatives whose constitution could be settled. Recently there has been quite a considerable activity in this field.

Copaene.—In view of the modified structure for cadinene, the structure of copaene, which yields cadinene dihydrochloride on treatment with hydrochloric acid gas, has also been reinvestigated and shown to be (LIX)[5]. Copaene on ozonolysis yields a monobasic ketonic acid, $C_{13}H_{24}O_3$, which can be represented by (LX). This acid on further oxidation with Na hypobromite yielded a dibasic acid regarded by Semmler and Stenzel[72] as $C_{13}H_{18}O_4$; this is not understandable on the basis of the formulation (LX) for the ketonic acid. This aspect requires reinvestigation[73]. Another important point has been raised by Birch[74] who has indicated that (LXI) is one of the several other possible structures which cannot be excluded on the present evidence.

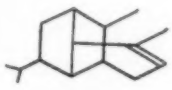
Work now on hand at Bangalore[75] will soon clarify the situation.



(LIX)



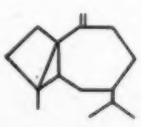
(LX)



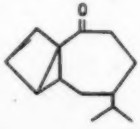
(LXI)

Aromadendrene.—Aromadendrene is the principal sesquiterpene occurring in the eucalyptus oils. It is a tricyclic hydrocarbon with one double bond, which is known to be exocyclic from the various oxidation studies. On dehydrogenation with sulphur it gives *s*-guaiazulene.

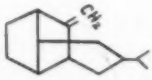
Recently Treibs and Barchet[76] have investigated the problem and have thrown considerable light on its structures. They have put forward the structure (LXII). On ozonolysis it yielded the crystalline ketone $C_{14}H_{22}O$, aromadendrone, which can be represented by (LXIII). Birch[74] has pointed out a number of objections to this



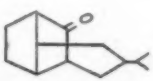
(LXII)



(LXIII)



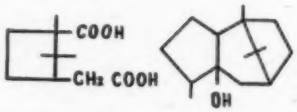
(LXIV)



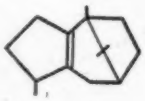
(LXV)

formula. For example, the action of amyl nitrite on aromadendrone does not yield an oximino derivative but an oximino-carboxylic acid in good yield, and hence probably it does not contain a CH_2 group adjacent to the carbonyl. He has further suggested that aromadendrene can be best represented by (LXIV) when aromadendrone will become (LXV). A deterimnation of the infra-red spectrum of aromadendrone may enable one to distinguish between (LXIII) and (LXV)[75].

Patchouli Alcohol.—Treibs[77] has oxidised patchoulene, obtained by the dehydration of the alcohol and has isolated a mixture of camphoric and homocamphoric acid (LXVI). Since patchouli alcohol on dehydrogenation gives *s*-guaiazulene and patchoulene is somewhat difficult to reduce catalytically, he has advanced the structure (LXVII) for the alcohol and (LXVIII) to the dehydration product.



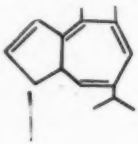
(LXVI) (LXVII)



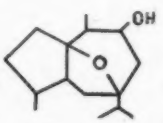
(LXVIII)

Since patchouli alcohol yields a mixture of hydrocarbons on dehydration, the formula (LXVIII) represents one of the three possible isomers.

Kessyl Alcohol.—Considerable light on its structure has also been thrown by Treibs[78]. Asahina[79] has shown that kessyl alcohol is a *s*-guaiazulene derivative containing a secondary hydroxyl and an oxide ring. Treibs oxidised the hydroxyl group and the carbonyl, the position of which was fixed by treatment with methyl-magnesium iodide, followed by dehydrogenation, when, 5-methylazulene (LXIX) was isolated, the structure of which was deduced on the basis of its absorption spectra. A number of transformations based on the fission of the oxide ring are described and (LXX) is considered to be the most appropriate representation for kessyl alcohol.



(LXIX)



(LXX)

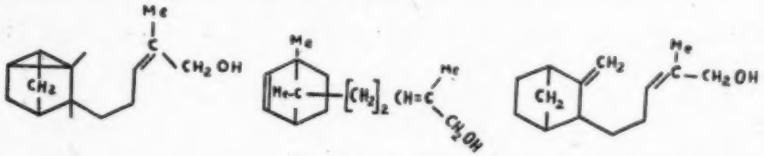
Santalols.—The chief constituent of East Indian sandalwood oil is a mixture of two primary alcohols termed α- and β-santalol. The former is tricyclic, whereas the latter is bicyclic in structure, and could have been treated under "bicyclic sesquiterpenes" but due to its close relation to α-santalol, both are best described together.

Santalols (α and β) have recently been obtained in a very pure state[80].

The structure (LXXI) for α-sanatol was arrived at several decades ago by Semmler and Bode[81] and has now been cofirmed by a strightforward synthesis by Guha and Bhattacharyya[82] starting from camphor. Guerbet's acid and α-santalic acid have been shown to be different, a probable structure for the former has been suggested[83].

The relationship between α- and β-santalol has been beautifully demonstrated by Bhattacharyya[84], who has described a direct conversion of α-santalol into β-santalol.

On the basis of degradation studies, two structures, viz. (LXXII, Simonsen[85]) and (LXXIII ; Ruzicka[86]) for β-santalol have been put forward. The recent synthesis by Bhattacharyya[87] confirms the structure by Ruzicka.



(LXXI) LXXII) (LXXIII)

Conclusion

India, with its variety of climate and soil, is exceptionally rich in the essential oil bearing plants. Sesquiterpenes and their derivatives constitute an important portion of some of these essential oils, e.g. cadar wood oil, gurjun balsam oil, cedrala toona oil, etc. It is quite possible that some of these products can find direct application in industry, but it appears to be essential that suitable modifications in the molecular structure of the natural components and their degradation products will have to be carried out to produce more useful materials. The fields of synthetic perfumery material, insecticides, high polymers, etc. appear to be especially promising domains. Further research work will sometime be necessary to settle the structural details of the chief components, before any plan to put them to industrial applications. It will be, however, ideal if any factory, already engaged in the manufacture of synthetics and isolates, could take up such work. This will, however, require a great foresight on the part of the industrial management.

My sincere thanks are due to Dr. Sukh Dev for compiling some of the references.

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[Jour. Indian Chem. Soc., Vol. 30, No. 2, 1953]

MOLYBDENUM CARBONITRIDE

By S. P. Ghosh

A ternary alloy containing molybdenum, nitrogen and carbon has been prepared and its structure has been elucidated by X-ray analysis.

Ternary metal—carbon—nitrogen systems have received very little attention. Deville (*Compt. rend.*, 1868, **66**, 83) claimed to have prepared a niobium carbonitride of the formula *m*NbN-*n*NbC by heating Nb_2O_5 with Na_2CO_3 in a graphite crucible at 1200°. Agte and Moers (*Z. anorg. Chem.*, 1931, **198**, 233) have found by X-ray diffraction the existence of mixed crystals in the system TiC—TiN and TaC—TaN. Stackelberg *et al.* (*Z. physikal. Chem.*, 1935, **175**, 127) obtained a compound, Al_3C_3N by the interaction of aluminium and carbon in presence of nitrogen at 1800°. Hausler (*Z. anorg. Chem.*, 1926, **154**, 333) found that UC_2 could be completely converted into the nitride by heating in nitrogen at 1100°. No X-ray examination was made in this investigation. It is probable that an intermediate uranium carbonitride is formed. It has been shown by Riley (*Quart. Rev.*, 1949, III, 169) that there is a close crystallographic similarity between carbon and nitrogen and there should be a large number of intermediate phases containing both carbon and nitrogen in different alloy systems.

These intermediate phases could be prepared either by carbiding a nitride or nitriding a carbide. There is no mention of molybdenum carbonitride in the literature. In the present work an investigation on the formation of molybdenum carbonitride was made by carbiding molybdenum nitride.

Experimental

The apparatus used was the same as used for the preparation of molybdenum nitride (this *Journal*, 1952, **29**, 484). The circulatory pump used was designed by J. Gibson and others (*J. Sci. Inst.*, 1946, **24**, 137). The pump incorporates a metal bellow and is connected to a valve system. In order to remove any CO_2 formed during the reaction, the system was provided with two condensation bulbs which were kept immersed in liquid oxygen. An outlet was also provided in the condensation system for taking out samples of gas for analysis.

A known amount of the nitride was taken in a silica boat and kept in the cold part of the reaction tube. The whole system was then evacuated and the furnace heated to the desired temperature. Pure CO was then admitted to the system. The pressure inside the system was maintained at the atmospheric level. Any CO_2 remaining as impurity with the CO was condensed in the condensation bulb. Thus the whole system was filled with pure CO. The volume of the gas as shown in the gas burette was noted before starting the experiment. The boat was then placed in the proper place inside the furnace with the help of the solenoid. The volume of the gas was noted every 10 minutes and the reaction continued till the disappearance of CO was negligible.

The volume of the gas consumed could not be determined accurately from the burette readings because of many variables; but it provided a rough idea of the gas intake. In the process of carbiding a nitride it is probable that the nitrogen atoms expelled may escape as cyanogen or nitrogen. After every run the CO_2 bulbs were heated up and the expelled gas was absorbed in caustic alkali. These solutions were found to contain cyanogen and in some cases paracyanogen.

The mixed nitride (β and δ), containing 42.2 atomic% nitrogen, was first carbided between 450° and 730° with carbon monoxide. The following observation was made:

450° ... Reduction to metallic molybdenum, formation of oxides and a trace deposition of carbon.

500° ... Complete conversion into MoO_3.

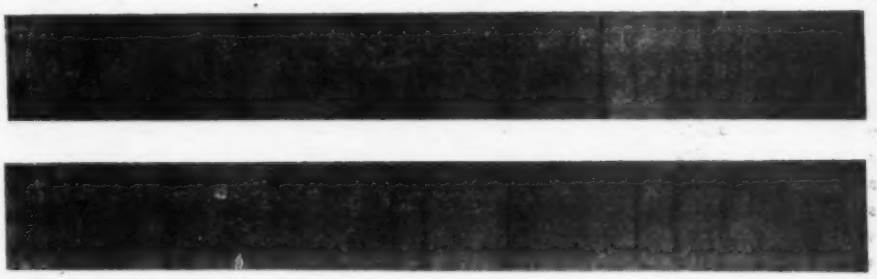
600°-730° ... No reaction.

Higher temperature was not tried as the nitride was unstable.

The γ-nitride with a nitrogen content of 32.2 atomic% nitrogen was then carburised at 450°. The result was oxide formation. There was no detectable reaction at 600°. At 700°, CO reacts with the nitride with the formation of a ternary Mo-C-N phase. In the X-ray photograph of the product the lines of the face-centered cubic nitride were shifted toward the centre (Fig. 1) due to an expansion of the lattice.

FIG. 1

Molybdenum carbonitride



Molybdenum nitride (γ)

It was found that with longer hours of carburising, as more carbon atoms went in replacing the nitrogen atoms, the lattice expanded more and more. But whilst there was a shifting of the lines of the γ-phase nitride, a new hexagonal phase also appeared. With higher carbon content this phase became more pronounced.

Table I shows the results of line measurement of a carburised nitride. The nitride originally contained 32.2 atomic % nitrogen. After 2 hours' carburising the nitrogen content was found to be 26.9 atomic% and the carbon content was found to be 6.7 atomic %.

TABLE I

Intensity.	$\sin^2\theta$ (obs.).	h k l.	$\sin^2\theta$ (calc.).
m	0.9159	420	0.9184
m	0.8712	331	0.8724
vw	0.7358	400	0.7347
w	0.5516	222	0.5510
ms	0.5059	311	0.5051
ms	0.3697	220	0 3673
s	0.1858	200	0.1836
s	0.1401	111	0.1377

The lines were indexed as face-centerd cubic. The value of a parameter was found to be 4.168Å. The original nitride had an a value = 4.144Å. So the increase in a value was 0.6%. The lines were, however, quite diffuse.

The same nitride was carbided for six hours; the product obtained contained 21.8 atomic% nitrogen and 15.7 atomic % carbon. Results of line measurements of a powder photograph are given in Table II.

TABLE II

Intensity.	$\sin^2\theta$ (obs.).	F. C. cubic		Hexagonal.	
		h k l.	Calc. $\sin^2\theta$.	h k l.	$\sin^2\theta$ (calc.).
m	0.9159	420	0.9172	003	0.9180
m	0.8706	331	0.8713		
w	0.7885	...	...	112	0.7905
w	0.7332	400	0.7337		
vw	0.6135	...	...	201	0.6120
w	0.5507	222	0 5503		
w	0 5342	...	...	102	0.5355
s	0.5053	311	0.5044		
m	0.4843	...	...	111	0.4855
w	0.3836	...	...	110	0.3825
s	0.3675	220	0.3668	...	
s	0.2315	...	...	101	0.2295
s	0.1803	200	0.1834		
vvw	0 1533	...	...		
s	0.1390	111	0.1375		
ms	0.1285	...	...	100	0.1275
m	0.1029	...	...	001	0.1020

It is found that one set of lines belongs to the cubic γ-phase. The value of a parameter = 4.183Å; increase in a is about 1%.

The other set of lines can be indexed as hexagonal of which the quadratic form is given by

$$\sin^2\theta = 0.1275\,(h^2 + hk + k^2) + 0.1020\,l^2$$

$$a = 2.888\text{Å},\ c = 2.800\text{Å} \text{ and } c/a = 0.969.$$

The hexagonal phase became more pronounced when the carbiding was done at 800°. But the carbonitride phase was also found to be present.

The γ-nitride was then carbided at 850°. At this temperature the hexagonal phase was produced to a large extent as only some low angle lines of the γ-phase, which appeared as strong lines in the nitride, appeared as only very weak lines. Results of line measurements are given in Table III.

TABLE III

Intensity.	$\sin^2\theta$ (obs.).	Hexagonal. $\sin^2\theta$ (calc.)	hkl.	F. C. Cubic. $\sin^2\theta$ (calc.)	hkl.	Intensity.	$\sin^2\theta$ (obs.)	Hexagonal $\sin^2\theta$ (calc.)	hkl.	F. C. Cubic. $\sin^2\theta$ (calc.)	hkl.
m	0.9236					vvw	0.5026	...		...	
m	0.9110	0.9090	003			s	0.4845	0.4850	111		
m	0.8889	...	...	0.8925	351	vw	0.4561	...	...		
m	0.8770	...				vw	0.4423	...	...		
vw	0.8633	...				w	0.4061	0.4040	002		
vw	0.8285	...				ms	0.3841	0.3840	110		
w	0.8003	...	...			vvw	0.3730	...	...	0.3557	220
s	0.7875	0.7880	112			vvw	0.3591	...	...		
vvw	0.7396	...	...			vvw	0.2948	...	...		
vvw	0.6457	...	...			vvw	0.2634	...	...		
s	0.6113	0.6130	201			vs	0.2307	0.2290	101		
vw	0.5555	...	...			m	0.1867	...	...	0.1878	200
s	0.5344	0.5320	102			vs	0.1294	0.1280	100		
s	0.5188	...	...	0.5167	311	ms	0.1028	0.1010	001		

There were quite a large number of weak and very weak lines which could not be indexed. A set of lines was indexed as satisfying the quadratic form:

$$\sin^2\theta = 0.1280\ (h^2 + hk + k_2) + 0.1010\ l^2$$

$$a = 2.883\text{Å},\ c = 2.830\text{Å} \text{ and } c/a = 0.981.$$

Thus, with the introduction of more carbon the c parameter has increased from 2.800Å to 2.830Å. The a parameter has slightly decreased.

The low angle lines of the γ-nitride phase were also present, but only as weak lines. A rough value of a parameter calculated from these was found to be 4.121Å. This value is much less than that of the γ-nitride (4.144Å). Probably this phase is the original nitride phase, the lower a value is due to lower nitrogen content.

From these experiments it is concluded that no ternary Mo—C—N phase can be produced from the $(\beta+\delta)$ mixed nitride. The γ-nitride froms an interstitial solid solution with carbon. This is supported by the expansion of the γ-nitride lattice on the replacement of nitrogen atoms by carbon atoms. The repalcement is, however, not systematic as more carbon atoms get into the lattice than the nitrogen atoms expelled.

It could not be decided whether the hexagonal phase produced in the carbiding of the nitride is an interstitial carbonitride phase. According to Tamman (*Z. anorg. Chem.*, 1922, **124**, 25) the β-molybdenum carbide has a hexagonal lattice with $c/a = 1.579$,

the carbon content being 5.08%. But in the case of the carbided product at 850°, the carbon content was 5.38% and the axial ratio, $c/a = 0.981$. Thus, it appears that it might be possible to produce a simple hexagonal carbide by carbiding the nitride in contrast to MoC_2 which has a close packed hexagonal lattice.

During the process of carbiding of the nitride the reaction, $2CO \rightarrow CO_2 + C_{atomic}$ occurred. There was very little tendency for the formation of graphitic carbon both in the case of the mixed $(\beta+\delta)$ and the γ-nitride. The same observation has been made by Jack (*Proc. Roy. Soc.*, 1948, **A, 195**, 41) in the case of iron nitride. This result supports the view expressed by Riley (*loc. cit.*) that carbon formation is not a surface phenomenon but occurs within the lattice.

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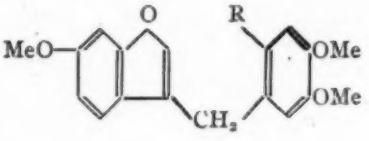
EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART II

By J. N. Chatterjea

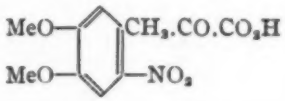
Attempts to prepare 3-benzylcoumarones of the type (I, R = acyl) designed for a different synthesis of β-brazans have not been successful. Contrary to the observations of Gilman and his coworkers, it is shown that the cyclisation of the acid (XI) gives a mixture of the ketones (XII) and (XIII) ; the former has been converted into 7-hydroxy- and 7-methyl-β-brazan. Experiments on the cyclisation of the pyruvic acid of the type (XVII, R″=CH_2.CO.CO_2H) to the γ-brazan (XV, R″=CO_2H) have been so far unsuccessful. However, the hydroxy-γ-brazan (XV, R=OMe, R′=Me, R″=OH) has been synthesised according to the method of Jhonson and Robertson.

In the preceding communication (this *Journal*, 1953, **30**, 1) it has been shown that 2-acyl-3-benzylcoumarones may be cyclised to β-brazans. An alternative route to the β-brazans is the cyclodehydration of 3-benzylcoumarones of the type (I, R=acyl) where the acyl group is in the benzene nucleus. Synthetical experiments in this direction were therefore undertaken.

For this purpose, 2-nitro-4: 5-dimethoxyphenylpyruvic acid (II) (Oxford and Raper, *J. Chem. Soc.*, 1927, 418) was converted into its oxime and then dehydrated with hot acetic anhydride to 2-nitro-4: 5-dimethoxyphenylacetonitrile (III). However, attempts to prepare the ketonitrile (IV) in pure condition by condensation of the nitrile with ethyl *m*-methoxyphenoxyacetate in alcoholic sodium ethoxide, have not



(I)



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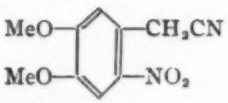

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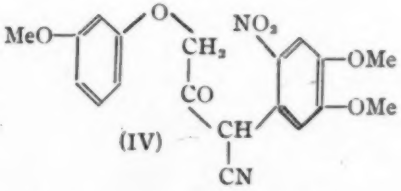
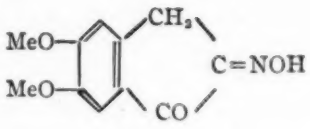


(IV)

been successful (cf. Avenarius and Pschorr, *Ber.*, 1929, **62**, 323) due probably to the acid hydrolysis of (IV) being rendered more facile by the substitution of the nitro group in the *ortho* position. Experiments on the synthesis of the equivalent intermediate (VIII) were next attempted. 2-Carboxy-4 : 5-dimethoxybenzylcyanide (VI, R=H) was conveniently prepared by the action of *p*-toluenesulphonyl chloride on 2-nitroso-5 : 6-dimethoxy-α-hydrindone (V) (cf. Haworth and Pink, *J. Chem. Soc.*,

1926, 1368) and then methylated with diazomethane in ether to the methyl ester (VI, R=Me). The Claisen condensation of methyl *m*-methoxyphenoxyacetate with this ester in alcoholic sodium methoxide afforded, very curiously, mainly the keto-nitrile



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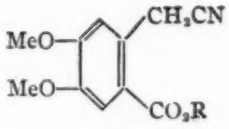

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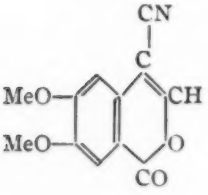

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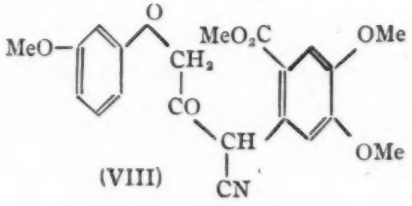

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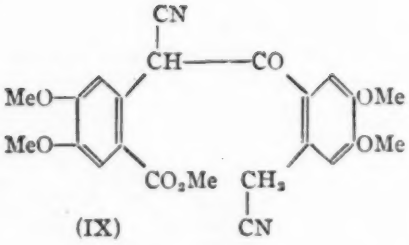
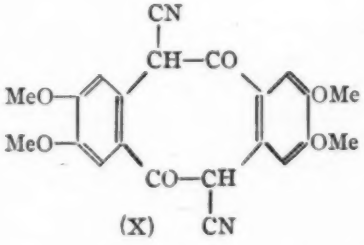


(IX)

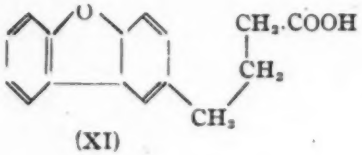


(X)

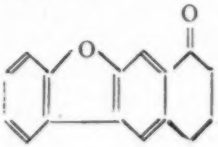
(IX) as a result of self-condensation of the methyl ester (VI, R=Me) together with a very small quantity of the expected product (VIII). As a result of the poor yield, the project could not be pursued further. The condensation of (VI, R=Me) with methyl formate, however, gave wholly the expected *iso*coumarin (VII) (cf. Robertson *et al.*, *J. Chem. Soc.*, 1950, 3378). An attempt to cyclise the keto-nitrile (IX) with sodium ethoxide to the eight-membered compound (X) was unsuccessful.

A synthesis of β-brazan successfully exploited by Mosettig and Robinson (*J. Amer. Chem. Soc.*, 1939, **61**, 1150) was from γ-(2-dibenzofuryl)-*n*-butyric acid (XI) which on cyclisation with phosphoric oxide in phosphoric acid gives a mixture of ketones (XII) and (XIII) in which the former predominates. Contrary to the observations of Gilman *et al.* (*ibid.*, 1939, **61**, 2842) who found (XII) as the sole product of cyclisation of (XI) with sulphuric acid, it is now found that both the ketones (XII) and (XIII) are really formed in which former is again the main product. On reaction with methylmagnesium iodide, this ketone (XII) gave 7-methyl-7:8-dihydro-β-brazan which on dehydrogenation with palladised charcoal furnished 7-methyl-β-

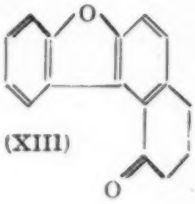
brazan (XIV, R=Me). Dehydrogenation of the ketone itself with palladised charcoal afforded a poor yield of 7-hydroxy-β-brazan (XIV, R=OH).



(XI)



(XII)



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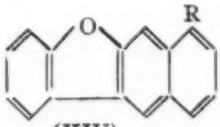
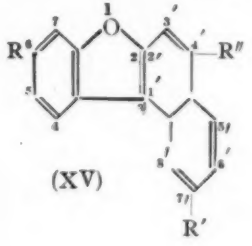


(XIV)

Exploratory experiments on the synthesis of γ-brazans of the type (XV, R″=H) by the cyclodehydration of appropriate 3-phenylcoumarone-2-pyruvic acid (XVII, R″=$CH_2.CO.CO_2H$) were carried out. 2: 4-Dihydroxy-3′-methylbenzophenone (XVI, R=OH, R′=Me, R″=H) (Bhagwat and Sahane, *Chem. Abs.*, 1940, **34**, 5071) was conveniently prepared by the Friedel-Crafts reaction of *m*-toluyl chloride with resorcinol in nitrobenzene (cf. Jhonson and Robertson, *J. Chem Soc.*, 1950, 2381). This was monomethylated with methyl iodide and potassium carbonate to 2-hydroxy-4-methoxy-3′-methylbenzophenone (XVI, R=OMe, R′=Me, R″=H) and then converted into 2-*m*-methylbenzoyl-5-methoxyphenoxyacetic acid (XVI, R=OMe, R′=Me, R″=CH_2CO_2H) by ethyl bromoacetate and potassium carbonate in acetone, followed by hydrolysis.



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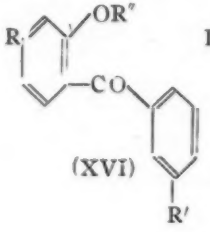
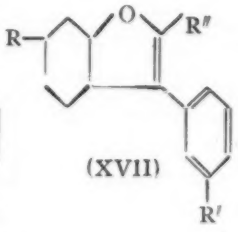
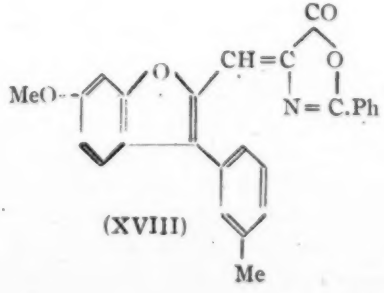


(XVI)



(XVII)



(XVIII)

On treatment with sodium acetate and hot acetic andydride, this phenoxyacetic acid gave 6-methoxy-3-*m*-methylphenylcoumarone (XVII, R=OMe, R′=Me, R″=H). On the Gattermann reaction with the aid of zinc chloride, this coumarone gave 2-formyl-6-methoxy-3-*m*-methylphenylcoumarone (XVII, R=OMe, R′=Me, R″=CHO) which on condensation with hippuric acid in the usual way gave the azlactone (XVIII). On alkaline hydrolysis, this compound gave a very poor yield of 6-methoxy-3-*m*-methylphenylcoumarone-2-pyruvic acid (XVII, R=OMe, R′=Me, R″=$CH_2.CO.CO_2H$). Attempts to cyclise this acid with glacial phosphoric acid or with hydrochloric acid in acetic acid were unsuccessful (cf. Birch and Robinson, *J. Chem. Soc.*, 1944, 503; Geissmann and Tess, *J. Amer. Chem. Soc.*, 1940, **62**, 514; Horning and Koo, *ibid.*, 1951, **73**, 5829).

The pyruvic acid on oxidation with alkaline hydrogen peroxide gave 6-methoxy-3-*m*-methylphenylcoumarone-2-acetic acid (XVII, R=OMe, R′=Me, R″=$CH_2.CO_2H$) which was prepared in quantity from the aldehyde (XVII, R=OMe, R′=Me, R″=CHO). This on oxidation with hydrogen peroxide gave 6-methoxy-3-*m*-methylphenylcoumarone-2-carboxylic acid (XVII, R=OMe, R′=Me, R″=CO_2H) which on homologation by the Arndt-Eistert procedure furnished (XVII, R=OMe, R′=Me, R″=$CH_2.CO_2H$) by way of the amide (XVII, R=OMe, R′=Me, R″=$CH_2.CONH_2$). The coumarone-2-acetic acid on cyclisation according to Jhonson and Robertson (*loc. cit.*), however, afforded the hydroxy-γ-brazan derivative, 6-methoxy-4′-hydroxy-7-methylnaphtho (2′:1′-2:3) coumarone (XV, R=OMe, R′=Me, R″=OH).

Further experiments on the cyclisation of the keto-nitrile (IX) and analogous compounds are in progress.

Experimental

(Unless otherwise mentioned all m.p.s are uncorrected.)

2-Nitro-4:5-dimethoxyphenylpyruvic acid was prepared according to Oxford and Raper (*loc. cit.*) by the action of ethyl oxalate on 6-nitrohomoveratrole in the presence of potassium ethoxide in dry benzene. After the isolation of the pyruvic acid, the benzene residue on evaporation gave a mixture of unchanged 6-nitrohomoveratrole and a compound which was probably sym.-*di*-(2-*nitro*-4:5-*dimethoxyphenyl*)*ethane*. The latter, which is sparingly soluble in alcohol, was easily purified and obtained in small, yellow prisms, m.p. 205°. (Found: C, 55.0; H, 5.2; N, 7.0. $C_{18}H_{20}O_8N_2$ requires C, 55.1; H, 5.1; N, 7.1 per cent). The compound did not decolorise bromine in acetic acid.

The *oxime* of the above pyruvic acid was obtained by adding hydroxylamine hydrochloride (11 g.) in small portions with stirring to an ice-cold solution of the α-ketonic acid (27 g.) in sodium hydroxide (150 c.c., 8%). The purple colour of the solution disappeared. The solution was allowed to stand for 24 hours when a solid (sodium salt of the oxime) appeared. The whole was acidified and the oxime crystallised from aqueous alcohol. It was obtained in thick yellowish plates (25 g.), m.p. 168° (decomp.). (Found: N, 9.8. $C_{11}H_{12}O_7N_2$ requires N, 9.9 per cent).

2-Nitro-4:5-dimethoxybenzyl Cyanide (cf. Niederl and Ziering, *J. Amer. Chem. Soc.*, 1942, **64**, 885).—The above oxime (1 part) was dehydrated by adding it carefully in small portions to warm acetic anhydride (3 parts). After the vigorous exothermic reaction was over, acetic anhydride (and acetic acid) was removed as far as possible in vacuum, and alcohol added to the residue when light yellow plates of the compound (50%) appeared. It was obtained from alcohol in nearly colorless plates, m.p. 110°. (Found: C, 54.5; H, 4.7. $C_{10}H_{10}O_4N_2$ requires C, 54.0 ; H, 4.5 per cent). On warming with alkali the compound gave a red solution ; a deeper colour was obtained with alcoholic sodium ethoxide.

2-Carboxy-4:5-dimethoxybenzyl Cyanide.—A solution of the *iso*nitroso compound (V, 1.4 g.) in sodium hydroxide (15 c.c., 10%) was gradually treated with constant stirring with *p*-toluenesulphonyl chloride (2 g.) at the room temperature and the solution completed by warming the mixture slightly on the water-bath. The solution was cooled, filtered, acidified and the resulting solid crystallised from dilute alcohol. The product (VI, R=H) (0.64 g.) was obtained in long, colorless needles, m.p. 164-65° (cf. Haworth and Pink, *loc.cit.*, m.p. 164-65° ; Robertson *et. al.*, *J. Chem Soc.*, 1950, 3378, m.p. 183.5°). The aqueous filtrate deposited on keeping a mixture of solids, identified as the unchanged (V) (0.14 g.) and 4 : 5-dimethoxyhomophthalic acid (0.2 g.) which were separated by taking advantage of the latter's solubility in acetic acid.

2-Carbomethoxy-4:5-dimethoxybenzyl Cyanide.—The above acid (VI,R=H) (3 g.) was finely powdered and suspended in dry ether (50 c.c.) and treated with an excess of ethereal diazomethane (from nitrosomethylurea, 3 g.). A vigorous evolution of nitrogen took place and the mixture was left overnight. Next day, the excess of diazomethane was decomposed with a few drops of acetic acid. The residue after removal of the ether was treated with dilute sodium carbonate solution (5%) and crystallised from methanol. The *ester* was obtained in colorless plates (or in prisms), m.p. 120-21°. (Found : C, 61.0; H, 5.3. $C_{12}H_{13}O_4N$ requires C, 61.3 ; H, 5.5 per cent).

Experiments on the Condensation of Methyl m-*Methoxyphenoxyacetate with 2-Carbomethoxy-4 : 5-dimethoxybenzyl Cyanide.*—To a solution of sodium methoxide (sodium, 0.2 g., methanol, 2.5 c.c.) was added with stirring a solution of methyl *m*-methoxyphenoxyacetate (2.0 g.) and 2-carbomethoxy-4 : 5-dimethoxybenzyl cyanide (1.95 g.) in dry methanol (2 c.c.). The mixture was refluxed on the water-bath for 2 hours and left overnight. Next day, the sodium salt was collected, washed with dry ether, dissolved in warm water and acidified with dilute acetic acid. The colorless solid (1.6 g.) on crystallisation from a large volume of methanol gave (IX) and obtained in beautiful colorless prisms, m.p. 263-64° (decomp.). (Found: C, 62.7; H, 5.3; N, 6.3, 6.4; OMe, 36.5. $C_{23}H_{22}O_7N_2$ requires C, 63.0; H, 5.0; N, 6.4 ; for 4 OMe + 1 COOMe, 35.4 per cent). The compound gives with dilute sodium hydroxide solution its sodium salt which gradually crystallises out. On treatment with ferric chloride in methanol the compound gives a faint green coloration and on keeping the solution deposits a yellow solid.

The methanolic mother-liquor after the filtration of (IX) slowly deposited a small quantity of a chalky precipitate which was purified by crystallisation from acetic acid. The compound is probably (VIII). It was obtained in nearly colorless prisms, m.p. 254° (decomp.). (Found: N, 2.9. $C_{21}H_{21}O_7N$ requires N, 3.5 per cent).

Hydrolysis of (IX).—The cyano-ketone (IX, 0.4 g.) was boiled with concentrated hydrochloric acid (60 c.c.) for 15 minutes and then further boiled with the addition of water (30 c.c.) and filtered. The filtrate deposited beautiful colorless leaflets (0.3 g.) which were collected and crystallised from boiling water (charcoal) or acetic acid. The product, which was probably the *amide* (IX, $CH_2.CONH_2$ in place of CH_2CN), was obtained in wooly mass, m.p. 240-42°. (Found: C, 60.3 ; H, 5.3 ; N, 6.8. $C_{23}H_{24}O_6N_2$ requires C, 60.5; H, 5.3; N, 6.1 per cent). The compound dissolves in sodium hydroxide with a green fluorescence. With alcoholic ferric chloride the compound gives a faint green coloration and on keeping the solution deposits a yellow solid. Further hydrolysis of the amide was done by boiling under reflux with dilute sodium hydroxide till the evolution of ammonia was over. The colorless solid obtained on acidification crystallised from water in overlapping prisms (or in plates), identified as 4:5-dimethoxyhomophthalic acid, m.p. and mixed m.p 223-24°. (Found: C, 54.6; H, 4.9. Calc. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0 per cent).

*4-Cyano-6:7-dimethoxy*isocoumarin (cf. Robertson *et. al., loc. cit.*).—To dry sodium methoxide from sodium (0.46 g.) and dry methanol were added in the cold with stirring, dry ether (50 c.c.), 2-carbomethoxy-4:5-dimethoxybenzyl cyanide (1 g.) and methyl formate (10 c.c.). Reaction took place immediately and a yellowish white precipitate separated gradually. The mixture was allowed to stand overnight and the next day it was refluxed for 1 hour. The solvent was removed completely, water added, filtered and acidified with warm concentrated hydrochloric acid. The copious precipitate of the iso*coumarin* (VII) (0.9 g.) was collected and obtained from acetic acid in slender, colorless needles, m.p. 298° (corr.). (Found: C, 62.4; H, 3.9; N, 5.6. $C_{12}H_9O_4N$ requires C, 62.4; H, 3.9; N, 6.1 per cent). The compound may be further purified by sublimation.

Cyclisation of γ-(2-dibenzofuryl)-n-butyric Acid (cf. Robinson and Mosettig, *loc. cit.* Gilman *et. al., loc. cit.*).—The acid was cyclised with sulphuric acid using Gilman's procedure. The crude product, on one crystallisation from alcohol had m.p. 127-30°. This was fractionally crystallised from benzene. The less soluble portion which contained (XII) was obtained in pure thick plates, m.p. 137° (lit., 137-38°). The oxime was obtained from alcohol in colorless prisms, m.p. 212-13° (lit., 212-13°). (Found: N, 5.5. Calc. for $C_{16}H_{13}O_2N$: N, 5.6 per cent).

The more soluble portion (m.p. *ca* 85°), on crystallisation from methanol, gave a mixture (m.p. *ca* 88-92°) consisting mica-like plates and hard prisms. These were separated mechanically and the prisms after two crystallisations from methanol gave (XIII) in a pure condition, m.p. 112-12.5° (lit., m.p. 112-13°); yield 2-3%. The oxime separated from pyridine-aqueous alcohol in colorless plates, m.p. 202.5° (lit., 202-203°). (Found: N, 5.5. Calc. for $C_{16}H_{13}O_2N$: N, 5.6 per cent).

The *2:4-dinitrophenylhydrazone* crystallised from nitrobenzene-alcohol in ochreous microcrystalline powder, m.p. 319° (corr.). (Found: N, 13.3. $C_{22}H_{16}O_5N_4$ requires N, 13.5 per cent).

7-Methyl-β-brazan.—To a solution of methylmagnesium iodide from magnesium (0.4 g.), methyl iodide (1.5 c.c.) in ether (30 c.c.) was added with stirring at the room temperature a solution of the ketone (XII) (3 g.) in dry benzene (20 c.c.). After the initial reaction was over, the mixture was heated under reflux for 4 hours. The mixture

was then treated with ice and dilute H_2SO_4, the ether layer separated, washed with water and concentrated, when a viscous liquid showing green fluorescence was obtained. On distillation, *7-methyl-7:8-dihydro-β-brazan* (2.5 g.) was obtained at 245°-248°/35 mm. (Found: C, 87.0 ; H, 6.1. $C_{17}H_{14}O$ requires C, 87.2 ; H, 6.0 per cent). The product (1.0 g.) was dehydrogenated with palladised charcoal (prepared according to Linstead and Thomas, *J. Chem. Soc.*, 1940, 1127) (0.1 g.) by heating in a metal-bath the temperature of which was slowly raised from 210° to 310° in course of 2 hours. The mass was extracted with benzene and the product (7-methyl-β-brazan, 0.8 g.) was obtained from benzene-alcohol in nearly colorless needles, m.p. 117°. (Found: C, 87.7; H, 5.2. $C_{17}H_{12}O$ requires C, 87.9; H, 5.2 per cent). The product may be purified by sublimation.

Although β-brazan does not give a picrate, this methyl derivative gives an unstable picrate, m.p. 126-27°. (Found: N, 9.2. $C_{17}H_{12}O.C_6H_3O_7N_3$ requires N, 9.1 per cent).

7 Hydroxy-β-brazan.—The ketone (XII, 0.5 g.) was intimately mixed with palladised charcoal (0.1 g.) and heated in a metal-bath at 250°-260° for ½ hour. The crude product was extracted several times with warm sodium hydroxide (5%), filtered and the greenish solution on acidification gave 7-hydroxy-β-brazan (0.06 g.), crystallising from benzene in colorless needles, m.p. 221-22°. (Found: C, 82.0; H, 4.6. $C_{16}H_{10}O_2$ requires C, 82.1; H, 4.3 per cent). The compound gives a violet-red azo dye with benzenediazonium chloride.

The *acetyl* derivative, prepared by the action of acetic anhydride and sodium acetate on the water-bath, crystallised from acetic acid in clusters of colorless needles, m.p. 145°. This was not analysed due to shortage of the material.

2:4-Dihydroxy-3'-methylbenzophenone was prepared by the condensation of resorcinol (32 g.) and *m*-toluyl chloride (40 g.) with aluminium chloride (38 g.) in nitrobenzene (325 c.c.) during 50 hours. The complex was decomposed with ice and hydrochloric acid and after removing nitrobenzene with steam, the residual solid (52 g.) crystallised from dilute alcohol, giving the *benzophenone* in pale yellow prisms, m.p. 170-71° (lit., 168°). (Found: C, 73.4; H, 5.5. Calc. for $C_{14}H_{12}O_3$: C, 73.7 ; H, 5.3 per cent). With ferric chloride it gives a red-brown coloration.

The *2:4-dinitrophenylhydarzone* separated from ethyl acetate in orange-red prisms, m.p. 293° (corr.). (Found: N, 13.6. $C_{20}H_{16}O_6N_4$ requires N, 13.7 per cent).

2-Hydroxy-4-methoxy-3'-methylbenzophenone.—Methyl iodide (2.0 c.c.) was added dropwise to a solution of the above-mentioned ketone (6 g.) and potassium carbonate (10 g.) in boiling acetone (50 c.c.) during 20 minutes, and the mixture heated under reflux for 1½ hours. On isolation, the resulting crude material was boiled twice with sodium carbonate solution (2*N*) which removed the unchanged ketone. The residue was then extracted with sodium hydroxide (2 × 65 c.c., 5%). The alkaline solution on acidification gave the product as an oil (4.1 g.), isolated with ether. This was dried in the desiccator and employed without further purification.

The alkali-insoluble portion solidified quickly giving *2:4-dimethoxy-3'-methylbenzophenone* (*ca.* 0.4 g.) crystallising from dilute alcohol (90%) in colorless prisms, m.p.

81-82°. (Found: C, 74.7; H, 6.1. $C_{16}H_{16}O_2$ requires C, 75.0; H, 6.2 per cent). The 2:4-*dinitrophenylhydrazone* separated from ethyl acetate in beautiful orange prisms, m.p. 170°. (Found: N, 13.3. $C_{22}H_{20}O_6N_4$ requires N, 12.8 per cent).

2-m-*Methylbenzoyl-5-methoxyphenoxyacetic Acid.*—A mixture of the foregoing phenol (5 g.), ethyl bromoacetate (4.2 c.c.), anhydrous potassium carbonate (14 g.) and acetone (50 c.c.) was boiled under reflux for 6 hours. On isolation the resulting ethyl 5-methoxy-2-*m*-methylbenzoylphenoxyacetate was obtained as an oil which was hydrolysed with boiling aqueous alcoholic potash (KOH, 10g. alcohol, 50 c.c. and water, 30 c.c.) during ½ hour. After removing alcohol in vacuum, the mixture was diluted with water (80 c.c.) and acidified. The resulting oil solidified affording the compound which separated from benzene-petroleum ether in colorless long needles, m.p. 80-81°. (Found: C, 68.1; H, 5.5. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.3 per cent).

6-*Methoxy*-3-m-*methylphenylcoumarone.*—A mixture of the above phenoxyacetic acid (2.5 g.), sodium acetate (5 g.) and acetic anhydride (20 c.c.) was heated at 160° (oil bath) for ½ hour. A brisk reaction was noted in the beginning. The product obiained by the addition of water was extracted with ether, washed with sodium bicarbonate and dried (sodium sulphate). The compound was obtained as a solid (1.8 g.), m.p. 29-30°. (Found: C, 80.2; H, 5.8. $C_{16}H_{14}O_2$ requires C, 80.6; H, 5.9 per cent). The compound does not give a crystalline picrate. With sulphuric acid it gives an orange-yellow coloration.

2-*Formyl*-6-*methoxy*-3-m-*methylphenylcoumarone.*—A solution of the foregoing coumarone (18 g.) and anhydrous hydrogen cyanide (25 c.c.) in ether (270 c.c.) containing zinc chloride (4 g.) was saturated with dry hydrogen chloride at 0° and next day, the crystalline product washed with dry ether and hydrolysed with water (500 c.c.) on the water-bath for 45 minutes when a greenish solid was obtained. This was collected and on crystallisation from alcohol, the *aldehyde* was obtained in long colorless needles, m.p. 106-107°, yield 16.5 g. (Found: C, 76.2; H, 5.5. $C_{17}H_{14}O_3$ requires C, 76.6; H, 5.3 per cent). The brown-red solution of this aldehyde in sulphuric acid became green (yellowish) and on dilution with water it became green and then blue.

The *oxime* crystallised from methanol in hard prisms, m.p. 101° (evolution of gas) with previous shrinking. (Found: C, 70.5 ; H, 5.4. $C_{17}H_{15}O_3N$. $\frac{1}{2}CH_3OH$ requires C, 70.7; H, 5.7 per cent).

6-*Methoxy*-3-m-*methylphenylcoumarone*-2-*pyruvic Acid.*—A mixture of the above aldehyde (3 g.), hippuric acid (2 g.), sodium acetate (1 g.) and acetic anhydride (20 c.c.) was heated on the steam-bath for ½ hour, cooled and diluted with aqueous alcohol (60 c.c., 50%). Crystallised from benzene, the resulting *azlactone* (XVIII) (3.9 g.) was obtained in small yellow needles, m.p. 205-207°. (Found: N, 3.6. $C_{26}H_{19}O_4N$ requires N, 3.4 per cent). This compound was hydrolysed with aqueous alcoholic potash (potassium hydroxide, 5 g., alcohol, 25 c.c. and water, 25 c.c.) in an oil-bath for 6 hours. In the beginning, light yellow needles appeared. After removing the tarry meterial by decantation, the solution was cooled, saturated with sulphur dioxide and left overnight. Next day, the mixture was filtered and the filtrate heated with concentrated hydrochloric acid on the water-bath when a yellow precipitate (0.04 g.) of the pyruvic

acid appeared. This was crystallised from ethyl acetate-petroleum ether and obtained in light yellow, tiny needles, m.p. 190° (decomp.). (Found : C, 70.0; H, 5.2. $C_{19}H_{16}O_5$ requires C, 70.4; H, 5.0 per cent). The compound gives a violet ferric chloride reaction.

6-*Methoxy*-3-m-*methylphenylcoumarone*-2-*acetic Acid* : *Method* (*a*).—Oxidation of the above-mentioned pyruvic acid (0.02 g.) in sodium hydroxide (5 c.c., 2%) with hydrogen peroxide (0.5 c.c., 30%) at the room temperature during 45 minutes furnished the compound which crystallised from benzene-petroleum ether in colorless needles, m.p. 132-33°. With sulphuric acid, the compound gave a deep yellow solution which on warming and on keeping turned green.

Method (*b*).—Hydrogen peroxide (5 c.c., 30%) was added dropwise to a stirred solution of the aldehyde (0.5 g.) in acetone (50 c.c.) in the presence of sodium hydroxide (10 c.c., 5%) at 40° for 1 hour. After removal of the acetone, the cooled reaction mixture was diluted with water, filtered from the gummy material and acidified giving a precipitate of the carboxylic acid (0.22 g.), crystallising from ethyl acetate-petroleum ether or from glacial acetic acid in slender, colorless needles, m.p, 190° (decomp.). This gave with sulphuric acid a deep yellow solution which on warming turned deep green. (Found: C, 72.1; H, 5.2. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0 per cent). The acid (3.8 g.) was converted into the acid chloride by means of phosphorus pentachloride (4 g.) in chloroform (80 c.c.) by warming on the steam-bath. The green solution on concentration in vacuum gave the acid chloride which solidified. A solution of the product in dry benzene (15 c.c.) was added dropwise to a solution of diazomethane (from 20 g. nitrosomethylurea) in ether (200 c.c.) at -2°. Next day, the solution was filtered from a spongy mass (polymethylene ?) and the solvent removed in vacuum. The *diazoketone* crystallised from benzene-petroleum ether in yellow prisms, m.p. 99° (decomp.), yield 2.9 g. (Found : N, 9.2. $C_{18}H_{14}O_3N_2$ requires N, 9.1 per cent). A solution of the diazo-ketone in dioxane (80 c.c.) was added dropwise to a well stirred solution of silver nitrate (40 c.c., 10%) in concentrated aqueous ammonia (25 c.c.) kept at 72°. After leaving at this temperature for 1 hour, next day the mixture was filtered, poured on a large volume of cold water and the crystals collected after 4 hours. Crystallised twice from ethyl acetate-petroleum ether, the 6-*methoxy*-3-m-*methylphenylcoumarone*-2 *acetamide* was obtained in colorless, slender needles (1.8 g.), m.p. 151-52°. (Found: N, 5.0. $C_{18}H_{17}O_3N$ requires N, 4.8 per cent). This amide (1.7 g.) was hydrolysed by boiling under reflux on the steam-bath with aqueous alcoholic potash (20 c.c., 10%) for 8 hours. After removing alcohol, the cooled residue diluted with water (75 c.c.), clarified by norite, filtered and acidified giving 6-methoxy-3-*m*-methylphenylcoumarone-2-acetic acid, crystallising from benzene-petroleum ether in colorless needles, m.p. and mixed m.p. 132-33°, yield 1.3 g. (Found: C, 72.7; H, 5.6. $C_{18}H_{16}O_4$ requires C, 72.9; H, 5.4 per cent).

6-*Methoxy*-4′-*hydroxy*-7′-*methylnaphtho*- (2′:1′-2:3)*coumarone*.—Phosphoric oxide (3.5 g.) was added with stirring during 3 minutes to a warm solution of the above acid (0.6 g.) in benzene (20 c.c.). The mixture was refluxed for 3 hours, decomposed with ice and extracted with ether.—The ethereal solution after washing with sodium bicarbonate was dried and evaporated leaving the *naphthocoumarone* as a pale yellow solid.

Crystallised twice from acetic acid, the compouud was obtained in almost colorless needles (o.3 g.), m.p. 164-66° giving a deep red and then green coloration with sulphuric acid. (Found: C, 77.5; H, 5.o. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.o per cent).

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INVESTIGATION ON VISCOSITY OF EMULSIONS

By R. K. Neogy and B. N. Ghosh

Viscosities of xylene emulsions stabilised with sodium oleate, myristate, laurate, capriate and saponin have been measured in a rotary viscometer. The viscosities depend a great deal on the nature of the emulsifier used. Different viscosity equations have been tested and Richardson's equation with a slight modification has been found to fit the experimental data best.

In a previous communication (this *Journal*, 1952, **29**, 573) viscosities of emulsions stabilised with cetyldimethylbenzylammonium chloride, cetylpyridinium bromide, cetyltrimethylammonium bromide and magnesium oleate have been recorded. It has been shown therein that of all the viscosity equations, those of Sibree and Richardson fit the experimental data best. Viscosity of xylene emulsions made with a few other soaps e.g., sodium oleate, myristate, laurate, capriate and saponin are recorded in this paper.

Experimental

The arrangement for the measurement of viscosity and temperature control has been described in the previous paper (*loc. cit.*). Sodium oleate has been prepared by the method of Berkman (*J. Phys. Chem*, 1935, **39**, 528). Oleic acid was converted into barium oleate and dissolved in ether. The ethereal solution was decomposed by HCl, oleic acid extracted with ether and dried over Na_2SO_4. Ether was evaporated off and oleic acid distilled at a reduced pressure. To the pure oleic acid in alcohol equivalent amount of sodium ethoxide was added when sodium oleate was precipitated. The precipitate was filtered, recrystallised from alcohol, finally washed with dried ether and kept in a vacuum desiccator. It was later found that instead of purifying oleic acid through barium salt, the same result could be obtained by distilling oleic acid twice or thrice under reduced pressure. Oleic acid in alcohol can be neutralised with alcoholic caustic soda instead of sodium ethoxide. The solution after neutralisation is evaporated on the water-bath and then taken in alcohol. Two or three recrystallisations from alcohol, followed by ether washing give practically a pure product of m.p. 228-29°. The myristic, lauric and capric acids and saponin were obtained from Eastman Kodak Company. The sodium salts of the three acids were prepared and purified in the same way as sodium oleate. Sodium stearate and palmitate have also been tried but they are sparingly soluble in water. An 1 or 0.5% solution can be prepared in hot water but on cooling it sets to a gel. Emulsions have been prepared in the usual way. Xylene was purified by fractional distillation and dried over fused $CaCl_2$.

To ascertain the effect of the emulsifying agents, viscosity of xylene emulsions stabilised with sodium oleate, myristate, laurate, capriate and saponin were measured in a rotary viscometer at 30°. For each viscosity measurement 5 or 6 readings were taken by varying the rates of shear. In the following tables (I-V) the mean viscosity as well as the viscosities at the minimum and maximum rates of shear are given. (The

mean viscosity is taken as the average of 5 or 6 viscosities taken at different rates of shear). It is to be noted, however, that maximum viscosity is not necessarily obtained at the maximum rate of shear. The data are summarised in Table VI.

TABLE I

1% *Sodium oleate–xylene system.*

Vol. % of xylene.	Rate of shear.		Shearing stress × 100.		η in c. p.			Yield value
	Min.	Max.	Min.	Max.	Min	Max.	Mean.	
10	4 62	30.04	28 3	131.0	3.96	4 03	3.97	0.1
20	16 64	43 91	118	309	6 49	6 81	6.71	0.1
30	12 48	28.65	141	299	10.5	10 09	10 37	0 1
40	16 64	34.20	260	528	14 42	14 85	14 66	0.2
50	11.55	22 64	239	453	18.05	19.13	19 07	0.2
60	12.48	35 98	360	10 10	27 28	26.74	26.99	0.2
80	7.85	14.79	1468	1914	65.98	65.24	65.40	9.5

TABLE II

1% *Sodium myristate–xylene system.*

Vol. % of xylene.	Rate of shear.		Shearing stress × 100.		η in c.p.			Yield value.
	Min.	Max	Min.	Max.	Min.	Max.	Mean.	
10	22 18	32 35	173.3	159.6	4.66	4.62	4.63	0.1
20	13.86	26.80	105.6	188.0	6 00	6.64	6.74	0.1
30	13 86	30.04	170	355.0	11.54	11 48	11.50	0.1
40	9.70	26 80	159.6	401.7	14 39	14.24	14.28	0.2
50	16.64	27.73	340	561	19.23	19.52	19 28	0 2
70	6.47	2c.11	448	978	38.33	38.69	38 41	2.0

TABLE III

1% *Sodium laurate–xylene system.*

Vol. % of xylene.	Rate of shear.		Shearing stress × 100.		η In c.p.			Yield value
	Min.	Max.	Min	Max.	Min.	Max.	Mean	
10	12.02	36.51	41 19	100.4	2.59	2.48	2 52	0.1
40	12 48	25 43	152 0	283.0	10 58	10 35	10.54	0.2
50	9.70	16 17	182.8	291 0	16.90	16.77	16.78	0.2
60	9.24	30 04	239.5	730.7	23.74	23.95	23.74	0.2
80	11.55	19 41	997.4	1517.0	64.42	65 28	64.74	2.5

TABLE IV

2% *Sodium crapriate–xylene system.*

Vol. % of xylene.	Rate of shear.		Shearing stress × 100.		η in c p.			Yield value.
	Min.	Max.	Min.	Max.	Min.	Max.	Mean.	
10	19.87	39 75	59 2	105 5	2.48	2.40	2.45	0.1
20	23.11	37 43	131 3	213 7	5.25	5 44	5 33	0.1
30	16.64	33 74	154.0	291.0	8 68	8.33	8 51	0.1
40	8.32	23.57	115.9	301.3	11 53	11.90	11.71	0.2
50	11.55	26.80	195.6	433.7	15 20	15.59	15 38	0.2
60	11.55	23 80	296.1	597.4	23.91	24.26	24 06	0.2

TABLE V

2% *Saponin – xylene system.*

Vol. % of xylene.	Rate of shear.		Shearing stress × 100.		η in c p.			Yield value
	Min.	Max.	Min.	Max.	Min.	Max.	Mean.	
10	9.24	47.14	114.0	438.0	9.09	8.66	8.82	0.03
20	12.02	26.57	306.0	644.0	22.13	22.69	22.59	0.4
30	18.05	35.59	842.0	1488.0	40.21	39.56	39.73	0.8
40	10.63	30.04	762.0	1936.0	62.32	61.20	61.60	1.0
50	11.09	30.50	1100.0	2863.0	88.39	89.95	88.78	1.2
60	3.69	18.49	932.0	3476.0	171.3	171.8	171.4	3.0

TABLE VI

Viscosity of xylene emulsions stabilised with different emulsifiers.

Vol. % of xylene.	1% Na oleate (0.033 *N*).	1% Na myristate (0.04*N*).	1% Na laurate (0.05 *N*).	2% Na capriate (0.103 *N*).	0.5% Saponin
10	3.57(0.10)	4.63(0.10)	2.52(0.10)	2.45(0.10)	8.82(0.30)
20	6.71(0.10)	6.74(0.10)	...	5.33(0.10)	22.59(0.40)
30	10.37(0.10)	11.50(0.10)	...	8.51(0.10)	39.73(0.80)
40	14.65(0.20)	14.28(0.20)	10.54(0.20)	11.71(0.20)	61.60(1.0)
50	19.07(0.20)	19.28(0.20)	16.78(0.20)	15.38(0.26)	88.78(1.2)
60	26.99(0.20)	...	23.74(0.20)	24.06(0.20)	171.4 (3.0)
70	39.27(4.0)	38.41(2.0)	...	...	...
80	65.40(9.5)	...	64.74(2.5)	...	...

Figures within bracket indicate yield values.

TABLE VII

0.5% *Saponin – paraffin oil system.*

Vol. % of oil	Rate of shear.		Shearing stress × 100.		η in c. p.			Yield values.
	Min.	Max.	Min.	Max.	Min.	Max.	Mean.	
20	9.24	22.18	327.0	623.0	23.48	23.13	23.37	1.1
30	16.17	36.51	842.0	1643.0	39.68	39.53	39.57	2.0
40	9.24	23.11	832.0	1720.0	62.96	63.60	63.03	2.5

TABLE VIII

2% *Saponin – paraffin oil system.*

Vol. % of oil.	Rate of shear.		Shearing stress × 100.		η in c. p.			Yield values.
	Min.	Max.	Min.	Max.	Min.	Max.	Mean.	
20	13.30	32.35	463.0	914.0	23.36	23.61	23.43	1.5
30	9.24	25.43	595.0	1256.0	39.49	40.34	39.97	2.3
40	4.62	18.49	538.0	1430.0	62.34	63.83	63.21	2.5

TABLE IX

Vol. % of oil.	η with 0.5% saponin.	η with 2% saponin.
20	23.37	23.43
30	39.57	39.97
40	63.03	63.21

It will be noted from the data recorded in Table VI that the viscosity of emulsions depends a great deal on the nature of the emulsifier used. Saponin emulsions have viscosities greater than those of the soap-stabilised emulsions. Emulsions stabilised with laurate and capriate have viscosities slightly less than those of oleate and myristate Another point of interest is, that barring saponin, the difference in the viscosities of the emulsions diminishes as the proportion of the dispersed phase is increased. As regards stabilising capacity it is found that sodium capriate is decidedly a much weaker emulsifier than the others. When the dispersed phase is 40 to 50% of the total volume, 1% capriate does not produce an emulsion, while the other soaps at the same concentration give a stable emulsion. After capriate, comes the laurate while for the other soaps and saponin, it is rather difficult to compare their emulsifying power. Emulsions with cetyl salts are least viscous, are formed practically spontaneously and are quite stable, thus the common view that the increase of viscosity increases the stability by hindering the coalescence of drops cannot be justified in this case.

The variation of viscosity with the nature of an emulsifier is rather difficult to explain, but it may be assumed that the interfacial film which stabilises the emulsion plays the vital role for this change in viscosity. The question may be raised that as we have considered the effect of soaps in terms of percentages and not in terms of molecular proportion, the results may not be strictly comparable. On careful analysis it will be found that this does not affect our conclusion. The concentrations of oleate and myristate used (1%) are respectively 0.033N and 0.04N, yet their viscosities are more or less the same. The normalities of laurate and capriate are 0.045 and 0.1031 but they do not affect the resulting viscosity. To establish this point beyond doubt, experiments were carried out using paraffin oil as the internal phase and saponin (2% and 0.5%) as the emulsifier. The data are recorded in Tables VII—VIII while Table IX gives the summarised results.

The data in Table IX show clearly that the viscosity of emulsions with widely varying concentrations of saponin is nearly the same. Hence, it can be inferred with a fair degree of accuracy that substitution of molar concentration in place of percentage concentration will not affect the conclusions already arrived at.

Referring to Table VI, it is observed that the yield values increase with the increase in the concentration of the dispersed phase. In most of the systems the yield values are rather small and do not change appreciably up to 60% of the dispersed phase. After this, it rises sharply with further increase in concentration of the internal phase.

Experimental Test of the various Viscosity Equations

Various viscosity equations have been discussed in the previous paper (*loc. cit.*). It is proposed to test further the applicability of these equations to the data recorded in this paper. Viscosity of soap solutions and saponin has been measured as usual in an Ostwald viscometer. The viscosities obtained in c. p. at 30° are sodium oleate (1%), 0.8482; sodium laurate (1%), 0.8433; saponin (0.5%), 0.8531; sodium capriate (2%), 0.8482.

Viscosity of sodium myristate at 30° cannot be measured as at this temperature gelation occurs. It has already been stated in the previous paper that Einstein's

and Hatschek's equations are not applicable to any one of the systems studied and the kind of deviation is illustrated with sodium oleate–xylene system in Table X.

Sibree's equation $$\eta = \frac{\eta_0}{1 - \sqrt[3]{k\varphi}},$$

Richardson's simple equation $\frac{\eta}{\eta_0} = e^{k\varphi}$ and

Richardson's modified equation (cf. Neogy and Ghosh, *loc. cit.*) $\frac{\eta}{\eta_0} = e^{(k\varphi + c)}$

were also examined. It is found that only Richardson's modified equation can represent the results to an accuracy of 5%. The other two equations fail miserably. Tables XI—XIII illustrate this.

TABLE X

Sodium oleate–xylene system.

φ represents phase volume ratio.

Vol. % of xylene.	Values calculated from Einstein's eqn. $\eta = \eta_0(1 + 2.5\,\phi)$	Values calculated from Hatschek's eqn. $\eta = \frac{\eta_0}{1 - \sqrt[3]{\phi}}$	Observed values.
10	1.060	1.584	3.97
20	1.273	2.043	6.71
30	1.485	2.565	10.37
40	1.696	3.223	14.66
50	1.908	4.113	19.07
60	2.120	5.420	26.99

TABLE XI

Sodium oleate-xylene system.

Vol % of xylene.	Observed values of $\log \eta/\eta_0$.	Calculated values of $\log \eta/\eta_0$ from Sibree's equation $\eta = \eta_0 \frac{1}{1 - \sqrt[3]{1.3\,\phi}}$	Richardson's equation. $(K = 3.09)$†	Richardson's modified eqn. $(K = 1.7,\ c = 0.54)$
10	0.6703	0.3068	0.309	0.71
20	0.8982	0.4417	0.618	0.88
30	1.0872	0.5689	0.927	1.05
40	1.2377	0.7080	1.2377	1.22
50	1.3512	0.8735	1.545	1.39
60	1.5029	1.1002	1.854	1.56
70	1.6655	1.51	2.163	1.73
80	1.8871	...	2.472	1.90

TABLE XII

Sodium laurate–xylene system.

Vol. % of xylene,	Observed values of $\log \eta/\eta_0$.	Calculated values of $\log \eta/\eta_0$ from Sibree's equation.	Richardson's equation ($K=2.742$)†	Richardson's modified eqn. ($K=2.0$, $c=0.28$).
10	0.4754	0.3068	0.2742	0.48
40	1.0969	0.7080	1.0969	1.08
50	1.2988	0.8735	1.3710	1.28
60	1.4494	1.1002	1.6452	1.48
80	1.8852	...	2.936	1.88

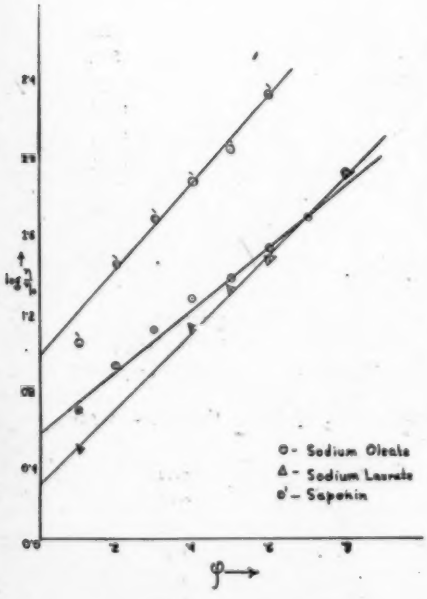
TABLE XIII

Saponin–xylene system.

Vol % of xylene.	Observed values of $\log \eta/\eta_0$.	Calculated values of $\log \eta/\eta_0$ from Sibree's equation.	Richardson's equation. ($K=4.65$)†	Richardson's modified equation. ($K=2.23$, $c=0.96$).
10	1.0145	0.3068	0.465	1.183
20	1.4229	0.4417	0.930	1.406
30	1.6681	0.5689	1.395	1.629
40	1.8586	0.7080	1.8586	1.852
50	2.0173	0.8735	2.325	2.075
60	2.303	1.1022	2.790	2.298

† The values of K in Richardson's original equation have always been calculated from 40% emulsion.

Fig. 1



Sibree's claim that his equation is applicable when the concentration of the dispersed phase exceeds 50%, does not seem to be justified. On plotting $\log \eta/\eta_0$ against φ a straight line is obtained (Fig. 1) but it does not pass through the origin in any case. This conclusively shows that Richardson's simple equation is not correct, but his modified equation is correct. The values of 'k' and 'c' as found from the plots are given in Tables XI—XIII.

The values of c varies with the soap used, thus it is 0.54, 0.28 and 0.96 for emulsions stabilised with sodium oleate, laurate and saponin respectively.

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COMPLEX SALTS OF BENZAMIDOXIME WITH METALS

By Debabrata Bandyopadhyay

Complex compounds of copper, palladium, cobalt and nickel with benzamidoxime have been described and their magnetic properties studied. Nickel forms an insoluble red compound which is converted by alkalies into a highly soluble deep blue salt.

It has been shown that the red nickel complex does not contain any tripositive nickel atom, as represented by Dubský and co-workers but is, as usual, a derivative of bipositive nickel.

The action of iron^{III} chloride on benzamidoxime has also been studied.

Krüg (*Ber.*, 1884, **17**, 128, 1685; 1885, **18**, 1054) observed that benzamidoxime gave an intense red coloration with ferric chloride. Werner (*Ber.*, 1908, **41**, 1069) found that benzamidoxime gave a brown-green precipitate with a solution of copper^{II} salt. Dubský and co-workers (*Coll. Czech. Chem. Com.*, 1935, **7**, 1) described the preparation of a red nickel salt of benzamidoxime which was regarded by them as a salt of tervalent nickel on account of its liberating iodine from acidified potassium iodide solution. Based on analytical data it was assigned the composition $Ni\,[ON:\,(H_2N)C.C_6H_5]_3$. They also obtained a green copper salt of composition $C_6H_5.C(NH_2):NO.Cu\,(OH),H_2O$. The present paper deals with the preparation, properties and magnetic behaviour of copper, palladium, cobalt and two nickel salts. The action of iron^{III} chloride solution on benzamidoxime has also been studied.

The green coloured copper salt is quantitatively precipitated from a solution of copper chloride or copper sulphate by benzamidoxime at a p_H of about 6.5–6.7 in presence of sodium acetate. The substance has been found to be paramagnetic (μ_B = 1.23). The unusually low value of the magnetic moment indicates that the substance is probably a mixture of Cu^{II} and Cu^{I} salts of composition $C_6H_5.C\,(NH_2):NO.Cu'OH$ and $C_6H_5.C\,(NH_2):NO.Cu,\,H_2O$ respectively, due to partial reduction of cupric copper by the reagent (cf. Krüg, *loc. cit.*).

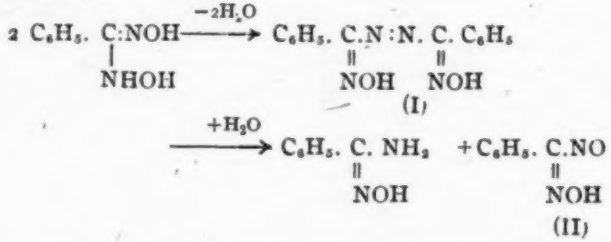
The palladium salt was obtained as a yellowish orange precipitate from a solution of palladium^{II} chloride in aqueous sodium chloride by the addition of the requisite quantity of the amidoxime solution. The substance is diamagnetic as is to be expected for a square planar palladium^{II} complex.

The cobalt compound was prepared from dichloro-tetrapyridine-cobaltic chloride and benzamidoxime in presence of a small amount of sodium hydroxide. The substance on drying forms a brownish black powder which is paramagnetic. This is rather unusual for a cobaltic compound since only a few cobaltic compounds, e.g , the oxide and the fluoride, are paramagnetic.

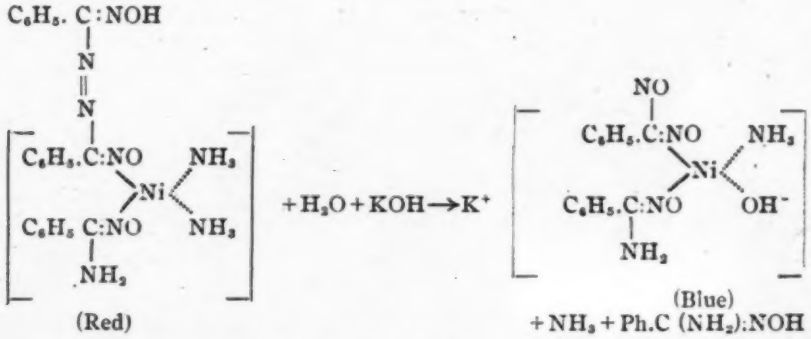
On treating an ammoniacal solution of nickel chloride with benzamidoxime the blue colour of the solution was gradually intensified and on being allowed to stand in contact with air for a day or two the mixture slowly deposited needle-shaped red crystals. These were found to liberate iodine from an acidified KI solution. When an aqueous suspension of the red salt was treated with dimethylglyoxime and a little ammonia, all the nickel was precipitated, and the clear filtrate retained the oxidising action of the original compound. This clearly shows that the red nickel complex contains bivalent nickel and that its oxidising action is attributable to the character of the ligand. Since benzamidoxime alone or in the presence of nickel salt in acid solution does not liberate

iodine from KI, the red nickel salt must have been derived from an oxidation product of the amidoxime, which is capable of liberating iodine from KI. The red salt, which is insoluble in water, dissolves in caustic alkalies and even in concentrated ammonia to form a deep blue solution from which a deep blue compound has actually been isolated by working in alcoholic medium. The deep blue colour appears instantaneously when a solution of nickel chloride, benzamidoxime and alkali is treated with any of the oxidising agents like hydrogen peroxide, lead dioxide, silver oxide, or potassium ferricyanide. Preliminary attempts to isolate the actual oxidation product of amidoxime have failed so far.

Reference might be made in this connection to the observations made by Wieland and Bauer (*Ber.*, 1906, **39**, 1480) that benzohydroxamoxime, $C_6H_5C(NHOH):NOH$, is converted by alkalies and even by ammonia into a red azo body (I) which is further hydrolysed to benzamidoxime and benzonitrosolic acid (II), and that the latter forms dark blue alkali salts.



Based on this observation it might reasonably be assumed that in presence of nickel as a catalyst, benzamidoxime is first of all oxidised by air to the azo compound (I) which forms the red nickel salt, and this is decomposed by alkali to give the blue nickel compound derived from benzonitrosolic acid (II) and benzamidoxime. Both (I) and (II) being oxidising agents might account for the oxidising action of the nickel complexes. The transformation of the red to the blue compound, by the action of alkali, may be represented as follows:



When a solution of nickel chloride, benzamidoxime, and ammonia is prepared with air-free water and kept in a securely stoppered vessel from which air has been removed by passing a current of hydrogen gas, no red compound is obtained. This shows that

the oxidation of the amidoxime is effected by air prior to the formation of the red nickel complex.

It was not possible to titrate the iodine liberated from potassium iodide by the red nickel salt as the end-point was rather fleeting and indefinite.

The red compound was found to lose ammonia on being treated with dilute alkali in the cold. It suffered no loss when dried over sulphuric acid *in vacuo*, indicating that the ammonia molecules are more or less firmly held inside the co-ordination zone.

Both red and blue nickel salts were found to be diamagnetic, as might be expected for square planar nickel^{II} complexes. It further disproves Dubsky's supposition that the red salt contains tripositive nickel atom.

When a solution of ferric chloride was added to that of an excess of benzamidoxime, there appeared a brown coloured precipitate, which dissolved in excess of ferric chloride to form a dark red solution. With sodium hydroxide or ammonia this red solution precipitated ferric hydroxide, while the clear filtrate gave usual tests for benzamidoxime. The presence of any oxidation product of the reagent could not, however, be detected in the filtrate.

EXPERIMENTAL

Benzamidoxime was prepared by refluxing benzonitrile (1 mol.), hydroxylamine hydrochloride (1 mol.) and sodium hydroxide (1 mol.) in alcoholic solution for 18 hours. The alcohol was then distilled off and the oily residue was dissolved in hot water, decolorised with activated charcoal, and filtered. The filtrate was concentrated and cooled in an ice bath till the separated oil crystallised out. This was filtered off, washed with ice-cold water, and purified by dissolving in benzene and then precipitating with petroleum ether. The product was recrystallised repeatedly from water, followed by a treatment with benzene and petroleum ether till it gave a definite m. p. 78-79° (Krüg, *loc. cit*). [Found: N, 20.39. Calc. for $C_6H_5.C(NH_2):NOH$: N, 20.59 per cent].

Copper Benzamidoxime.—A solution of copper^{II} chloride was treated with that of an excess of benzamidoxime and sodium acetate. The green coloured precipitate was filtered off, washed thoroughly with water and dried in air.

The substance is insoluble in water, soluble in acetic acid and mineral acids, as also in ammonia solution. The bluish green solution first formed in ammonia becomes colorless with an excess of the latter on account of reduction of cupric to cuprous state. On treatment with caustic alkalies the copper compound ultimately gives rise to cuprous oxide. The substance decomposes readily on heating and is paramagnetic. $\chi_g = 2.723 \times 10^{-6}$; $\chi_M = 614.7 \times 10^{-6}$; $\mu_B = 1.23$. [Found: Cu, 29.30; N, 12.95. $C_6H_5\,C(NH_2):NO.Cu(OH)$ requires Cu, 29.47; N, 12.99 per cent].

Palladium Benzamidoxime.—Palladium^{II} chloride, dissolved in an excess of sodium chloride solution, was treated with an aqueous solution of the requisite quantity of the amidoxime, and the mixture was allowed to stand for some time. The yellowish orange precipitate of the palladium complex was filtered off, washed first with 0.3% hydrochloric acid and then with water, and finally dried over calcium chloride for several days.

The substance is insoluble in water, soluble in acids and in ammonia, but not in caustic alkalies. It is diamagnetic. $\chi_g = -0.5018 \times 10^{-6}$. $\chi_M = -198.1 \times 10^{-6}$. {Found:

Pd, 26.94; N, 14.05. $Pd[ON:(H_2N)\ C.C_6H_5]_2,H_2O$ requires Pd, 27.03; N, 14.19 per cent}.

Cobalt Benzamidoxime.—An aqueous solution of $[Co(C_5H_5N)_4\ Cl_2]Cl,\ 6H_2O$ (1 mol.) was treated with that of benzamidoxime (3 mol.) in the cold. The green solution turned red. This was then carefully neutralised with sodium hydroxide when a blue precipitate separated out. The precipitate was filtered off, washed with cold water and dried over sulphuric acid *in vacuo*. The dried product is brownish black in colour.

The substance is insoluble in water but soluble in acids. When freshly precipitated it dissolves in alkalies to form a very deep blue solution. The substane is paramagnetic. $\chi_g = 17.96 \times 10^{-6}$; $\chi_M = 4130 \times 10^{-6}$; $\mu_B = 3.18$. [Found: Co, 25.68; N, 12.55. $C_6H_5.C(NH_2) : NO\ Co(OH)_2$ requires Co, 25.77; N, 12.23 per cent].

Red Nickel Compound.—An aqueous solution of nickel chloride (1 mol.) was treated with that of benzamidoxime (3 mol.) and to the mixture ammonia was gradually added till a clear solution was obtained. This was slightly warmed on the water-bath and then filtered. The clear blue filtrate was allowed to stand for several days in a loosely covered vessel, from which red shining crystals gradually separated. These were filtered off, washed first with ice-cold ammoniacal water, then with cold water and finally dried in air.

The substance is slightly soluble in cold water but decomposed by hot water. The aqueous solution reacts faintly alkaline. It is highly soluble in alcohol, acetone, and ether to form a ruby-red solution. It dissolves in caustic alkalies and in ammonia to form a deep blue solution. It is decomposed by acids and liberates iodine from acidified potassium iodide. When gently heated it suffers decomposition with the formation of a black residue. When treated with dilute caustic alkali solution the substance liberates ammonia even in the cold. The substance is diamagnetic. $\chi_g = -0.1394 \times 10^{-6}$; $\chi_M = -68.96 \times 10^{-6}$. [Found: Ni, 11.71; N, 22.41. {Ni $[C_6H_5.C\ (:NO)\ N:N-(HON:)\ C.\ C_6H_5]$ $[C_6H_5.C\ (NH_2):NO]\ (NH_3)_2$} requires Ni, 11.87; N, 22.64 per cent].

Blue Nickel Compound (potassium salt).—When the red nickel complex was treated with caustic potash in alcohol, a deep blue solution was obtained. A blue solid was precipitated from it by the addition of absolute ether. The product was dissolved in acetone and reprecipitated with ether. This was dried over calcium chloride and caustic potash.

The substance is highly soluble in water, alcohol and acetone. It is decomposed by acids and even by carbon dioxide. Its aqueous solution hydrolyses and reacts strongly alkaline. The substance is diamagnetic. $\chi_g = -0.3242 \times 10^{-3}$; $\chi_M = -134.8 \times 10^{-6}$. [Found: Ni, 14.32; K, 9.63; N, 17.14. {Ni $[C_6H_5.C\ (NH_2):NO]$ $[C_6H_5.C\ (NO):NO]-(OH)\ (NH_3)$} K requires Ni, 14.12; K, 9.39; N, 16.85 per cent].

The magnetic susceptibilities were measured by Gouy's method.

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5:6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT. PART III. ESTIMATION OF ZINC, COBALT, NICKEL AND MANGANESE

By Anil Kumar Majumdar and Anil Kumar De

The reagent 5:6-benzoquinaldinic acid has been used for the estimation of zinc, cobalt, nickel and manganese. The points of incipient precipitation for these elements are at about p_H 2.08, 2.14, 2.15 and 1.75 respectively and the respective p_H regions for their complete precipitation are at and over 2.85, 3.24, 3.00 and 2.90. The salt may be dried at 110°-115° and weighed as the hydrated salts, e.g., zinc, with one mole of water, cobalt with two, and both nickel and manganese with two and a half moles of water. The cobalt salt may also be dried at 150°-155° and wieghed as the anhydrous salt.

5:6-Benzoquinaldinic acid was used as a reagent for the estimation of copper and its separation from magnesium, calcium, strontium, barium, phosphate, arsenite, arsenate, citrate, tartrate etc. (Majumdar and Mallick, this *Journal*, 1952, **29**, 255) and also for the estimation of cadmium and its separation from copper (Majumdar and De, *ibid.*, 1952, **29**, 499). Both copper and cadmium were estimated at p_H over 0.82 and 3.12 respectively and almost all the elements were precipitated by the reagent under different p_H conditions. The present communication comprises the methods for the estimation of zinc, cobalt, nickel and manganese, the study of the p_H ranges over which they are accurately estimated, and the effect of temperature on their salts.

Zinc, cobalt, nickel and manganese are completely precipitated at and over p_H 2.85, 3.24, 3.00 and 2.90 respectively and they may be estimated gravimetrically in presence of mineral acids and acetic acid, ammonia and caustic alkali. Below the respective p_H mentioned above, they are incompletely precipitated due to solubility and their point of incipient precipitation from hot solution, being at about the p_H 2.08, 2.14, 2.15 and 1.75 respectively. The highly crystalline salts after precipitation and washing may be dried at 110°-115° and weighed as the hydrated salts; zinc as $Zn(C_{14}H_8NO_2)_2, H_2O$; cobalt as $Co(C_{14}H_8NO_2)_2, 2H_2O$ and both nickel and managanese as $M(C_{14}H_8NO_2)_2, 2.5\ H_2O$ (where M=Ni or Mn). The cobalt salt may also be dried at 150°-155° when due to loss of water, it may be weighed as the anhydrous salt.

Experimental

In addition to the reagents mentioned previously (*loc. cit.*), sodium hydroxide of different normalities and sodium acetate were used here. They were of reagent quality. Here also an 1% solution of sodium benzoquinaldinate (1 g. of the benzoquinaldinic acid of m.p. 187° per 100 c.c. of the solution) was used.

Standard solutions.—Kahlbaum's pro-analysi granulated zinc was dissolved in concentrated nitric acid (pro-analysi) and made up to the desired volume. The zinc content per c.c. of the solution was determined by estimating zinc as sulphate by drying at a temperature between 450° and 740° (cf. Duval and Clerq, *Anal. Chim. Acta*, 1951, **5**, 282) and as pyrophosphate.

Cobalt nitrate solution was prepared by dissolving cobalt nitrate (Merck & Co., Reagent) in a known volume of water. Cobalt in the solution was estimated electrolytically and also as sulphate by drying at 600°-812° (cf. Duval and Duval, *ibid.*, 1951, **5**, 84).

Schering-Kahlbaum's 'cobalt free' nickel sulphate was dissolved in a definite volume of water. Nickel in the solution was determined by dimethylglyoxime and by electrodeposition.

Manganese sulphate solution was obtained from manganese sulphate (E. Merck, pro-analysi) and standardised as sulphate by drying at a temperature between 200° and 940° (Duval and Dupuis, *ibid.*, 1949, **3**, 589).

Preparation and Composition of the Zinc, Cobalt, Nickel and Manganese Salts of 5:6-Benzoquinaldinic Acid.—The salts were prepared in the same way as described for copper and cadmium salts in previous communications (*loc. cit.*) and dried at 110°-115°. The dried salts were decomposed in the same way as was done in the case of cadmium (*loc. cit.*) and excepting nickel, other metals were estimated as the anhydrous sulphate. The nickel salt could not be estmated as the anhydrous sulphate as it decomposed to a basic salt (cf. Duval and Duval, *ibid.*, 1951, **5**, 71) and hence estimated as the dimethylglyoximate. Results of analysis of the compounds are shown below.

Metal found.	Calc. from.	Metal calc.
Zn, 12.41, 12.45	$ZnR^*.H_2O$	12.40%
Co, 10.92, 10.96	$CoR.2H_2O$	10.94
Ni, 10.69, 10.72	$NiR.2.5H_2O$	10.72
Mn, 10.08, 10.12	$MnR.2.5H_2O$	10.10

* $[R = (C_{14}H_8NO_2)_2]$

The zinc salt is white; cobalt, cream-coloured; nickel, greenish and manganese, yellow. All of them are soluble in excess of dilute acids and in cyanide. The zinc salt is soluble also in excess of ammonia and alkali. Cobalt, nickel and manganese salts, on the other hand, are insoluble in ammonia. In moderately strong caustic soda solution both the nickel and manganese salts are decomposed to their hydroxides, but the cobalt salt dissolves on heating and reappears on cooling. Like the copper and cadmium salts, they are all insoluble in organic solvents such as ethyl alcohol, amyl alcohol, ether, benzene, carbon disulphide and carbon tetrachloride.

Precipitation limits for Zinc, Cobalt, Nickel and Manganese.—The precipitation limits were found in the same way as in the case of copper and cadmium (*loc. cit.*). Precipitates were obtained even at a dilution of 1 part in 50, 0.5, 0.5 and 100 million parts respectively.

Effect of Temperature on the Salts.—The procedure was the same as given in earlier papers (*loc. cit.*). The zinc salt with 1 H_2O was stable up to 140° and then lost water till at about 186° it became anhydrous and in which state it was stable up to 260° (Clement Duval of Sorbonne, Paris, private communication). The salts of nickel and manganese, like zinc, were stable with 2.5 H_2O up to 140°. At 180° the nickel salt lost 7.23% of water and the manganese salt about 6.60%. The cobalt salt, on the other hand, lost water completely at 150° though up to 130° it was stable with 2 moles of water.

Like the salts of copper and cadmium (*loc. cit.*), the cobalt salt dried at 110°-115° and at 150°-155° was analysed as the anhydrous sulphate in the same way as described above. [Found: Co (dried at 110°-115°), 10.90, 10.94 ; Co (dried at 150°-155°), 11.74, 11.69 ; loss of water, 6.64, 6.71. Calc. for Co $(C_{14}H_8NO_2)_2$: Co, 11.72 ; loss of $2H_2O$, 6.68 per cent].

The results in Table I show that cobalt could be estimated according to the method given below either by drying at 110°-115° (to dihydrate) or at 150°-155° (to anhydrous salt).

TABLE I

No.	Cobalt taken.	Reagent soln.	p_H.	Dried at 110°-115°.		Dried at 150°-155°.	
				Co salt.	Co found.	Co salt.	Co found.
1	9.12 mg.	8.0 c.c.	3.93	83.4 mg.	9.12 mg.	77.8 mg.	9.12 mg.
2	9.12	8.0	5.52	83.4	9.12	78.0	9.14
3	9.12	8.0	8.95	83.2	9.10	77.7	9.11

Estimation of Zinc, Cobalt, Nickel and Manganese

The solution containing the metal ion was neutralised with dilute ammonia, using Wesselow's indicator, acidified with 1 c.c. of sulphuric acid ($N/10$) and diluted to about 200 c.c. It was then heated to boiling, precipitated with the reagent, digested, filtered etc. according to the method described in previous communications (*loc. cit.*) under copper and cadmium. Table II gives the data for zinc ; Table III, for cobalt ; Table IV, for nickel and Table V, for manganese.

TABLE II

Drying temp. = 110°-115°. Factor = 0.1240.

No.	Zn taken.	Reagent soln.	p_H.	Zn salt.	Zn found.	Error.
1	6.27 mg.	5.0 c.c.	3.67	50.6 mg.	6.27 mg.	Nil
2	10.04	8.0	3.66	80.9	10.03	−0.01 mg.
3	18.83	15.0	3.88	151.5	18.79	−0.04
4	25.10	20.0	3.70	202.4	25.10	Nil
5	37.65	30.2	3.75	304.0	37.70	+0.05

TABLE III

Drying temp. = 150°-155°. Factor = 0.1172.

No.	Co taken.	Reagent soln.	p_H.	Co salt.	Co found.	Error.
1	5.39 mg.	5.0 c.c.	3.72	46.0 mg.	5.39 mg.	Nil
2	9.70	9.0	3.70	82.8	9.70	Nil
3	21.56	19.8	3.70	183.6	21.52	−0.04 mg.
4	32.34	29.5	3.73	276.0	32.35	+0.01
5	43.12	39.0	3.76	368.6	43.19	+0.07

TABLE IV

Drying temp. = 110°–115°. Factor = 0.1072.

No.	Ni taken.	Reagent soln	p_H	Ni salt.	Ni found.	Error.
1	4.24 mg.	3.8 c. c.	3.70	39.5 mg	4.23 mg	−0.01 mg.
2	10.61	9.5	3.72	99.0	10.61	Nil
3	15.92	14.4	3.68	148.7	15.94	+0.02
4	21.22	19.0	3.72	197.8	21.20	−0.02
5	31.83	28.8	3.78	297.1	31.85	+0.02

TABLE V

Drying temp. = 110°—115°. Factor = 0.1010.

No.	Mn taken	Reagent soln.	p_H	Mn salt.	Mn found.	Error.
1	4.06 mg.	4.5 c.c.	3.70	49.2 mg.	4.97 mg.	+0.01 mg.
2	9.93	9.0	3.68	98.3	9.93	Nil
3	18.62	16.8	3.75	184.6	18.64	+0.02
4	24.82	22.5	3.70	246.0	24.85	+0.03
5	31.00	27.9	3.76	308.0	31.10	+0.10

TABLE VI

Drying temperature = 110°-115°.

No.	Zn taken.	Acetic acid (1 : 1).	$N/10$-H_2SO_4.	Sodium acetate.	Reagent soln.	p_H.	Zn salt.	Zn found.	Error.
1	10.02 mg.	2 c. c.	—	—	8.0 c. c.	3.45	80.8 mg.	10.02 mg.	Nil
2	,,	3	—	—	,,	3.20	80.8	10.02	Nil
3	,,	5	—	—	,,	2.85	80.4	9.97	−0.05 mg.
4	,,	6	—	—	,,	2.72	79.4	9.85	−0.17
5	,,	7	—	—	,,	2.50	77.0	9.55	−0.47
6	8.02	2	—	4 g.	6.5	4.95	64.6	8.01	−0.01
7	,,	4	—	4	,,	4.32	64.6	8.01	−0.01
8	,,	Just acidic	—	4	,,	6.70	64.7	8.02	Nil
9	10.02	—	2 c. c.	—	8.0	3.35	80.7	10.01	−0.01
10	,,	—	4	—	,,	2.95	80.8	10.02	Nil
11	,,	—	5	—	,,	2.75	79.8	9.90	−0.12
12	,,	—	6	—	,,	2.60	79.2	9.82	−0.20
13	8.02	—	Just acidic	4	6.5	6.72	64.6	8.01	−0.01
*14	,,	—	—	—	,,	7.85	64.5	8.00	−0.02
*15	10.19	—	—	—	8.2	9.38	82.0	10.17	−0.02
‡16	10.04	—	—	—	8.0	8.30	81.1	10.07	+0.03
‡17	10.04	—	—	—	,,	9.15	80.8	10.02	−0.02
‡18	10.19	—	—	—	8.2	9.56	82.1	10.18	−0.01

From the table it follows that zinc can be estimated from and above p_H 2.85. Determined up to p_H 9.56.

Study of p_H ranges.—The method followed was the same as given above and the acidity was adjusted after neutralisation by acetic acid or sulphuric acid to obtain different p_H ranges. For higher p_H regions, *i. e.*, over about p_H 7, either the solution containing any one of the elements was treated with 2 g. of ammonium chloride and

rendered alkaline with dilute ammonia (2*N*) or caustic soda (*N*/10) and then diluted and heated to boiling before the addition of the reagent, or to the solution was added the required quantity of the reagent first and then before dilution and boiling was rendered alkaline with dilute ammonia or caustic soda. The filtrate in each case was used for the measurement of p_H by Beckman p_H meter. The results for zinc, cobalt, nickel and maganese are given in Tables VI, VII, VIII and IX respectively.

TABLE VII

Drying temperature = 150°-155°.

No.	Co taken.	Acetic acid (1:1).	*N*/10-H_2SO_4.	Sodium acetate.	Reagent soln.	p_H.	Co salt.	Co found.	Error.
1	9.12 mg.	1 c. c.	—	—	8.2 c. c.	3.74	77.9 mg.	9.13 mg.	+0.01 mg.
2	,,	2	—	—	,,	3.50	77.8	9.12	Nil
3	,,	3	—	—	,,	3.24	77.5	9.08	−0.04
4	,,	4	—	—	,,	3.10	76.6	8.98	−0.14
5	,,	5	—	—	,,	2.88	74.6	8.74	−0.38
6	,,	2	—	4 c. c.	,,	5.02	78.0	9.14	+0.02
7	,,	Just acidic	—	4	,,	6.68	77.6	9.10	−0.02
8	,,	—	1 c. c.	—	,,	3.68	77.8	9.12	Nil
9	,,	—	2	—	,,	3.40	77.8	9.12	Nil
10	,,	—	3	—	,,	3.30	77.6	9.10	−0.02
11	,,	—	4	—	,,	2.94	77.0	9.02	−0.10
12	,,	—	Just acidic	2	,,	6.41	77.6	9.10	−0.02
13	,,	—	Do	4	,,	6.70	77.9	9.13	+0.01
*14	,,	—	—	—	,,	9.20	77.8	9.12	Nil
*15	,,	—	—	—	,,	9.75	77.8	9.12	Nil
‡16	8.62	—	—	—	7.8	8.12	73.6	8.63	+0.01
‡17	,,	—	—	—	,,	9.55	73.7	8.64	+0.02
‡18	10.23	—	—	—	8.2	9.82	87.3	10.23	Nil

From the table it is found that cobalt can be accurately estimated from p_H 3.24 to higher p_H ranges. Determined up to 9.82.

TABLE VIII

Drying temperature = 110°-115°.

No.	Ni taken.	Acetic acid.	*N*/10-H_2SO_4.	Sodium acetate.	Reagent soln.	p_H.	Ni salt.	Ni found.	Error.
1	10.61 mg.	1 c.c.	—	—	9.5 c.c.	3.74	99.2 mg.	10.63 mg.	+0.02mg.
2	,,	2	—	—	,,	3.54	99.0	10.61	Nil
3	,,	3	—	—	,,	3.30	99.0	10.61	Nil
4	,,	4	—	—	,,	3.15	98.6	10.57	−0.04
5	,,	5	—	—	,,	2.92	97.8	10.48	−0.13
6	,,	6	—	—	,,	2.70	96.3	10.32	−0.29
7	,,	2	—	4 g.	,,	5.05	99.1	10.62	+0.01
8	,,	Just acidic	—	4	,,	6.72	99.0	10.61	Nil
9	8.49	—	1 c.c.	—	7.70	3.72	79.3	8.50	+0.01
10	,,	—	2	—	,,	3.45	79.4	8.51	+0.02
11	,,	—	3	—	,,	3.25	79.2	8.49	Nil
12	,,	—	4	—	,,	3.00	78.8	8.45	−0.04
13	,,	—	5	—	,,	2.80	78.0	8.36	−0.13
14	,,	—	Just acidic	2	,,	6.45	79.1	8.48	−0.01
15	,,	—	,,	4	,,	6.72	79.2	8.49	Nil
*16	,,	—	—	—	,,	8.30	79.0	8.47	−0.02
‡17	,,	—	—	—	,,	10.30	79.1	8.48	−0.01
‡18	,,	—	—	—	,,	10.50	79.4	8.51	+0.02
‡19	,,	—	—	—	,,	11.00	79.2	8.49	Nil
*20	12.11	—	—	—	10.9	9.70	113.2	12.13	+0.02

From these results it follows that nickel can be accurately estimated from a p_H 3.0 to higher p_H regions. Determined up to 11.0.

TABLE IX

Drying temperature = 110°-115°.

No.	Mn taken.	Acetic acid (1:1).	$N/10$-H_2SO_4.	Sodium acetate.	Reagent soln.	p_H.	Mn salt.	Mn found.	Error.
1	8.69 mg.	1 c.c.	—	—	7.90 c.c.	3.72	86.0 mg.	8.69 mg.	Nil
2	,,	3	—	—	,,	3.32	86.0	8.69	Nil
3	,,	4	—	—	,,	3.14	86.1	8.70	+0.01
4	,,	5	—	—	,,	2.90	85.6	8.65	−0.04
5	,,	7	—	—	,,	2.50	81.0	8.18	−0.51
6	,,	Just acidic	—	4 g.	,,	5.10	85.8	8.67	−0.02
7	,,	,,	—	4	,,	6.58	86.1	8.70	+0.01
8	,,	—	1 c.c.	—	,,	3.68	86.0	8.69	Nil
9	,,	—	2	—	,,	3.48	85.9	8.68	−0.01
10	,,	—	3	—	,,	3.26	86.2	8.71	+0.02
11	,,	—	4	—	,,	2.98	85.8	8.66	−0.03
12	,,	—	5	—	,,	2.78	85.2	8.61	−0.08
13	,,	—	6	—	,,	2.62	84.0	8.48	−0.21
14	,,	—	Just acidic	2	,,	6.40	86.0	8.69	Nil
15	,,	—	,,	4	,,	6.74	86.0	8.69	Nil
*16	,,	—	—	—	,,	8.24	85.1	8.70	+0.01
‡17	,,	—	—	—	,,	8.62	86.2	8.71	+0.02
‡18	,,	—	—	—	,,	8.70	86.0	8.69	Nil
*19	9.84	—	—	—	8.8	8.45	97.6	9.85	+0.01
‡20	,,	—	—	—	,,	9.30	97.5	9.85	+0.01

It is evident from the table that manganese can be estimated from p_H 2.90 upwards. Determined up to 9.30.

In Tables VI to IX the marks (*) and (‡) indicate that those experiments were done in ammoniacal and alkaline solutions respectively.

Incipient Precipitations for Zinc, Cobalt, Nickel and Manganese.—Working with hot solutions of gradually increasing p_H values, incipient precipitations were observed at well defined acidities with the different metal complexes—manganese, 1.75; zinc, 2.08; cobalt, 2.14; nickel, 2.15 (cf. Majumdar and De, *loc. cit.*).

Further work on the use of the reagent is in progress.

The authors wish to express their sincere thanks to Prof. Clement Duval of the University of Sorbonne, Paris, for his kind interest and one of us (A.K.D.) gratefully acknowledges his indebtedness to Messers. Calcutta Chemical Co., Ltd., for the grant of a research fellowship.

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CONDENSATION OF KETONIC CARBONYL COMPOUNDS WITH CYANOACETIC ESTER IN PRESENCE OF PIPERAZINE DIACETATE

By Chittaranjan Raha

Piperazine diacetate is found to be effective and useful catalyst in the condensation of carbonyl compounds with ethyl cyanoacetate (Knoevenagel's reaction) since it can be recovered and purified after removal of the products of reaction. Examples of its application are given and new compounds formed in certain cases have been characterised and described.

Since ammonium and amine salts of organic acids are better catalysts than the free bases themselves, Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2327; 1941, **63**, 3452) introduced ammonium acetate in presence of acetic acid and many other catalysts as condensing agents in the Knoevenagel reactions. Knoevenagel himself used many salt catalysts in the reaction known after his name (*Chem. Zentrl.*, 1905, II, 76, 179, 726, 1071). The superior catalytic activity of salts in place of either the free acid or the free base in aldol-type reactions finds a ready explanation in Brönsted's extended theory of acidic and basic catalysis (Brönsted, *Chem. Rev.*, 1928, **59**, 2327). Ammonium acetate in presence of acetic acid found extensive application in the synthesis of alkylidene-cyanoacetic esters, but a great disadvantage of this catalyst lies in the formation of by-products (Cope *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 3452; Mukherji, this *Journal*, 1947, **24**, 91; Cragoe *et al.*, *J. Org. Chem.*, 1950, **15**, 381; Banerjee and Das Gupta, *J. Amer. Chem. Soc.*, 1952, **74**, 1318).

Bezzi and Cocco (*Chem. Abs.*, 1950, **44**, 5826[g]) used piperazine as one of the catalysts in the Knoevenagel condensations and reported high yields. The present author, however, failed to obtain good yields with carbonyl compounds other than those used by the above mentioned workers. The views of Brönsted (*loc. cit.*) and of Cope (*loc. cit.*) led the author to use piperazine diacetate in presence of acetic acid as a better catalyst in such reactions. Actually good yields were obtained in all cases. The new catalyst has the advantage that it does not form any by-product; further, it can be recovered from the aqueous solution after removal of the products of reaction and may be used again after crystallisation from water and subsequent drying.

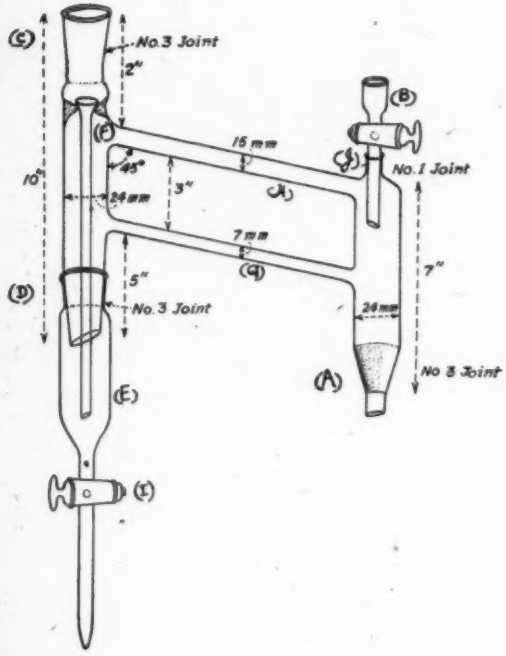
Based upon the views of Hahn and Lapworth (*J. Chem. Soc.*, 1904, **85**, 46) and of Hohler and Casson (*J. Amer. Chem. Soc.*, 1923, **45**, 1975), Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2329) formulated a mechanism for the Knoevenagel reactions catalysed by the salts which involved the generation of a carbanion from the compound containing reactive methylene group, followed by its addition to the carbonyl component and the subsequent elimination of a molecule of water from the transitory hydroxy compound formed by the addition of a proton to the negatively charged oxygen. The same mechanism should hold good in the reactions catalysed by piperazine diacetate.

Though the new catalyst succeeded in bringing about condensations involving cyanoacetic esters as much as and even better than ammonium acetate, it failed in con-

densing malonic esters with ketones and cyanoacetic esters with hindered ketones like camphor.

As described by Cope (*ibid.*, 1941, **63**, 3452) the reactions were carried out in flasks attached to a constant water separator (Dean and Stark, *Ind. Eng. Chem.*, 1920, **12**, 486). The water-separator (Fig. 1) used by the author has the reaction vessel attached to the st. joint (A) [No. 3 or B. 24]. The azeotropic system of benzene, acetic acid and water passes along (H), condenses in the condenser attached to the st. joint (C), falls along the thin and long funnel (F) in (E), a separatory funnel attached by st. joint at (D). The lower layer of water is taken out through the stop-cock (I). The upper layer of benzene flows back along (G) into the reaction flask at (A). (B) is a 25 ml. dropping funnel which is used to drop a liquid during the reaction. A solid reaction component may be added by detaching (B) from (J), a B-10 joint.

FIG. 1



This apparatus may be used for liquid-liquid extraction purposes with the funnel (F) reaching the bottom of the liquid-containing flask attached to (D). (A) carries the flask with the solvent, lighter than water. Other arrangements remain the same.

EXPERIMENTAL

Condensation of Ethyl β-Acetopropanoate and Ethyl Cyanoacetate in the presence of Piperazine.—To a mixture of ethyl β-acetopropanoate (43 g., 0.3 *M*) and ethyl cyanoacetate (35 g., 0.3*M*) in benzene (100 ml.) was added piperazine (1.5 g., 0.018*M*) and refluxed over a short free flame till the separation of water was complete (3 hours). The cooled, dark red solution was washed thrice with water, the solvent removed and the residual oil distilled under vacuum. The yield of the colorless liquid product was 27 g. (35% of theoretical); b.p. 160°/5.5 mm. (cf. Banerjee, this *Journal*, 1940, **17**, 423, b.p. 154°-160°/5.5 mm.).

Condensation of Ethyl β-Acetoglutarate and Ethyl Cyanoacetate : Piperazine Diacetate.—A mixture of ethyl β-acetoglutarate (10.3 g., 0.045*M*), ethyl cyanoacetate (5.6 g., 0.05*M*), piperazine (2.15 g., 0.025*M*), acetic acid (9 ml., 0.15*M*) and toluene

(80 ml.) was refluxed. Within an hour the separation of water was complete. Solid needles which sublimed during reflux on the upper cooler parts of the reaction vessel had m.p. 225-27° and mixed m.p. 228-30° with piperazine diacetate (m.p. 234°; Birkö-fer, *Ber.*, 1932, **75B**, 429). The cold solution was washed thoroughly with water, the solvent removed and distillation under vacuum yielded 8.5 g. (60% of theoretical) of a liquid, b.p. 125°-126°/1 mm. (Found: C, 58.85; H, 7.33; N, 4.41. Calc. for $C_{16}H_{23}O_6N$ C, 59.07; H, 7 07; N, 4.30 per cent).

The aqueous extract on evaporation gave piperazine diacetate, m.p. 230-31°.

Condensation of Ethyl β-Acetopropanoate and Ethyl Cyanoacetate.—To a mixture of ethyl β-acetopropanoate (30 g., 0.2*M*), ethyl cyanoacetate (30 g., 0.25*M*) and piperazine (10 g., 0.11*M*) in toluene (75 ml.) was added dropwise acetic acid with warming of the reaction mixture. The white flocculent precipitate of the piperazine diacetate, which first formed, gradually went into solution. Acetic acid (45 ml., 0.75*M*) was added in total. Complete separation of water required two and half hours. The dark red liquid was cooled, washed thoroughly with water. The water extract as before yielded piperazine diacetate. The hydrocarbon layer yielded 40 g. (85% of theoretical) of the desired condensation product, b.p. 98°/1.5 mm.

Attempts at the Condensation of Camphor with Ethyl Cyanoacetate: *'Lot addition technique' of Catalyst* (Cragoe *et al.*, *loc. cit.*). *Single solvent*: *Toluene.*—A mixture of camphor (5 g., 0.033*M*), ethyl cyanoacetate (4 g., 0.033 *M*), piperazine (0.3 g., 0.003 *M*), acetic acid (6 ml., 0.1 *M*) and toluene (75 ml.) was refluxed for one and half hours and a further amount of piperazine (0.2 g., 0.002 *M*), ethyl cyanoacetate (1.5 g., 0.01 *M*) and acetic acid (3 ml., 0.05 *M*) were added and refluxed for one hour. After a further addition of ethyl cyanoacetate (2 g., 0.015 *M*) and acetic acid (5 ml., 0.08 *M*) the mixture was refluxed for one hour more. On working up, the camphor was recovered unchanged.

An attempt to condense camphor with ethyl cyanoacetate by applying the portion-wise addition technique (Cragoe *et al.*, *loc. cit.*) of the catalyst in a solvent mixture of benzene, chloroform and xylene also failed to yield any product.

Camphor, however, has been condensed with ethyl cyanoacetate by the portionwise addition of ammonium acetate (cf. Cragoe, *et al.*, *loc. cit.*).

Attempts at the Condensation of Methylethyl Ketone with Diethyl Malo ate.—Methylethyl ketone (7.2 g., 0.1 *M*) together with diethyl malonate (16 g., 0.1 *M*), piperazine (1.7 g., 0.2 *M*), acetic acid (6 ml., 0.1*M*) in chloroform (60 ml.) was refluxed for 2 hours. The constituents were recovered unchanged.

Diethyl malonate could be condensed with reactive aldehydes in the presence of piperidine acetate (Cope *et al.*, *loc. cit.*). *cyclo*Hexanone was condensed with malonic ester in the presence of sodium ethoxide with sodium iodide catalyst (Giral and Guzman, *Ciencia*, 1946, **2**, 39). *cyclo*Pentanone was condensed with the same reagent in presence of acetic anhydride and aniline-zinc chloride complex (Kon, *J. Chem. Soc.*, 1926, 2727).

Condensation of Diethyl Acetone Dicarboxylate with Ethyl Cyanoacetate.—To diethylacetone dicarboxylate (44 g., 0.21 *M*), ethyl cyanoacetate (25 g., 0.22 *M*), acetic acid (10.5 ml., 0.2 *M*) in toluene (75 ml.) was added piperazine diacetate (prepared from piperazine, 3.7 g. and acetic acid, 5 ml.) and refluxed for one hour. On working up

the yield of the colorless liquid product was 20 g. (30% of theoretical), b.p. 155°/6 mm. (Found: C, 56.44; H, 6.99; N, 4.66. Calc. for $C_{14}H_{19}O_6N$: C, 56.55 ; H, 6.3 ; N, 4.71 per cent).

From the aqueous extract the catalyst was recovered.

**Condensation of Mesityl Oxide with Ethyl Cyanoacetate.*—To a refluxing solution of ethyl cyanoacetate (5.65 g.), acetic acid (2.5 ml.) in toluene (70 ml.) containing piperazine diacetate was added dropwise the freshly distilled mesityl oxide (5 g., 0.06 *M*) during 2½ hours. On working up a colorless, rubber-smelling liquid was obtained, yield 5 g. (55% of theoretical), b.p. 100°/4 mm. (Found: C, 67.86 ; H, 7.60 ; N, 7.31. Calc. for $C_{11}H_{15}O_2N$: C, 68.39 ; H, 7.77; N, 7.25 per cent).

Aqueous extract yielded some of the catalyst.

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* Knoevenagel condensation between an αβ-unsaturated ketone and a reactive methylene compound has been described by Knoevenagel (*loc. cit.*).

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STUDIES IN SURFACE TENSION MEASUREMENTS OF SOME COLLOIDAL SOLUTIONS. PART II. GELATIN SOL

By S. N. Banerji

The effect of concentration, temperature, acid, alkali and various salts on the surface tension of gelatin sols have been studied and the results have been explained from the point of view as given in earlier papers that lyophilic colloids such as gelatin, agar agar etc. have some dissolved material in a true molecular solution under the equilibrium :

Simple molecules $\rightleftharpoons$ aggregated molecules $\rightleftharpoons$ colloids.

It has been shown by some workers (Bottazzi, *Quart. J. Exp. Phys. Suppl.*, 1923, 65 ; Caro and Laporta, *Rend. Accad. Sci. Fis. Mat. Napon*, 1929, **35** 171) that gelatin produces a maximum depression of surface tension at the isoelectric point. The effects of concentration, temperature, acid, alkali and various salts on the surface tension of gelatin have been studied in this communication.

Experimental

The experimental procedure was the same as described in Part I of this series (this *Journal*, 1952, **29**, 270).

Purified gelatin (Goldruck, Kahlbaum) containing 0.1% ash was used. The gelatin foils were cut into strips and washed with cold water several times before use. Gelatin sols, prepared under different conditions, gave varying results. These were therefore prepared by dissolving purified gelatin in water on a warm bath kept at 80°. This gave concordant values for the same concentration of gelatin. The concentration of the sol was determined by evaporating a measured volume of it in a platinum crucible on a water-bath ; 1% of the sol, thus prepared, was of p_H value 5.7.

Table I

Effect of concentration on the surface tension of gelatin sol at 30°.

Surface tension of water at 30° = 71.03 (dynes / cm.).

Gelatin sol (%)	2.0	1.0	0.5	0.25	0.125
Surface tension (dynes / cm.)	63.24	64.21	64.72	65.20	65.80

Table II

Effect of temperature on the surface tension of gelatin sols of various concentrations.

	Surface tension at		
	30°.	40°.	50°.
Water	71.03	69.54	67.80
Gelatin (conc. %)			
0.5	64.72	61.93	60.54
0.25	65.20	63.90	62.62

TABLE III

Effect of HCl *of diff. conc. on the surface tension of gelatin sol at* 30°.

Sol.	Surface tension of gelatin sol. 0.5%.	1%.	2%.
40 c.c. sol + 10 c.c. water	65.19	64.93	64.03
40 ,, + ,, *N*/1.87-HCl	63.90	63.54	63.14
40 ,, + ,, *N*/94.5 ,,	65.20	63.90	63.00
40 ,, + ,, *N*/945 ,,	62.45	62.81	63.50
40 ,, + ,, *N*/1890 ,,	—	63.89	63 04

TABLE IV

Effect of NaOH *of diff. conc. on the surface tension of gelatin sol sat* 30°.

Sol.	Surface tension of gelatin sol. 0.5%.	1%.	2%.
40 c.c. sol + 10 c.c. water	651.9	64.93	64.00
40 ,, + ,, *N*/2.1-NaOH	68 50	66.51	66.06
40 ,, + ,, *N*/105 ,,	65.22	65.62	64.63
40 ,, + ,, *N*/1050 ,,	63.90	64.92	64.04

TABLE V

Effect of various salt solns. of diff. conc. on the surface tension of 10% *gelatin sol at* 30°.

Sol.	Surface tension.	Sol.	Surface tension
40 c.c. sol + 10 c.c. water	63.88	40 c.c sol + 10 c.c. *N*-NaCl	64 66
40 ,, + ,, *N*-LiCl	64.82	40 ,, + ,, 8.54 *N*- ,,	61.73
40 ,, + ,, 23.52 *N*- ,,	64.28	40 ,, + ,, 17.08 *N*- ,,	60.42
40 ,, + ,, 35.28 *N*- ,,	64.23	40 ,, + ,, 25.62 *N*- ,,	60.40
40 c.c. sol + 10 c.c. *N*-KCl	64.98	40 c.c. sol + 10 c.c. *N*-NH_4Cl	64 70
40 ,, + ,, 6.71 *N*- ,,	63.12	40 ,, + ,, 9.53 *N*- ,,	64.18
40 ,, + ,, 13 42 *N*- ,,	61.10	40 ,, + ,, 19.06 *N*- ,,	63 05
40 ,, + ,, 20.13 *N*- ,,	60.71	40 ,, + ,, 28.59 *N*- ,,	63.02

The results confirm the earlier observation (*loc. cit.*) that gelatin produces maximum depression of surface tension at the isoelectric point.

It is seen from the experimental results that the greater the concentration of the gelatin sol, the higher is the lowering of surface tension. This is in accord with the views given in previous papers (Banerji and Ghosh, this *Journal*, 1930, **7**, 923 ; Banerji, *loc. cit.*) that the lyophilic colloids such as gelatin, agar, agar etc. have some dissolved material in true molecular solution under the equilibrium

simple molecule $\rightleftarrows$ aggregated molecules $\rightleftarrows$ colloid.

At higher concentrations of gelatin sols, greater amounts remain dissolved giving rise to greater number of both aggregated and simple molecules and consequently there is a greater lowering of surface tension.

At the isoelectric point, the gelatin is at a maximum degree of aggregation and thus shows a maximum lowering of surface tension. The greater amount of acid may dissolve greater amounts of colloidal material and consequently there will be a greater number of simple molecules with the result that the surface tension values will not be lowered to a greater extent. High concentrations of acids depress dissociation of the aggregated molecules that are formed and the depression of surface tension will again be higher. The results obtained with 0.5%, 1% and 2% sols of gelatin support this conclusion. Ackermann (*Kolloid Z.*, 1934, **69**, 87) has observed that the surface tension of a gelatin sol decreases when the sol is boiled but it is raised by hydrolysis with acid. These observations are in line with the views given above.

The effect of alkali is to increase the surface tension continuously with the increasing concentration of alkali and the effect of solutions of different concentrations of monovalent salts in lowering the surface tension follows the order : $Na > NH_4 > Li > K$ in the case of gelatin sol.

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STUDIES IN SURFACE TENSION MEASUREMENTS OF SOME COLLOIDAL SOLUTIONS. PART III. TANNIC ACID, VANADIUM PENTOXIDE, ZIRCONIUM HYDROXIDE AND FERRIC HYDROXIDE SOLS

By S. N. Banerji

The surface tensions of tannic acid and of such hydrated and viscous sols as those of vanadium pentoxide, zirconium hydroxide and ferric hydroxide have been investigated at different concentrations and temperatures, both in presence and absence of electrolytes.

The experimental results indicate that the lowering of surface tension of water in the presence of a collodial substance originates from the presence of sufficient number of dissolved polaric and aggregated molecules.

In parts I and II of this series of papers (Banerji, this *Journal*, 1952, **29**, 270; 1953, **30**, 133), the results have been explained from the point of view that the reversible colloids such as gelatin, gum arabic etc. have some dissolved material in molecular condition under the equilibrium : simple molecules $\rightleftarrows$ aggregated molecules $\rightleftarrows$ collodial particles.

In this paper, the surface tensions of tannic acid and of such hydrated and viscous sols as those of vanadium pentoxide, zirconium hydroxide and ferric hydroxide have been investigated at different concentrations and temperatures, both in presence and the absence of electrolytes.

EXPERIMENTAL

The experimental procedure was the same as in the previous papers (*loc. cit.*).

Tannic Acid Sol.—A pure Kahlbaum's sample of tannic acid was used. γ stands for surface tension in dynes/cm.

TABLE I

Effect of concentration at 30°.

Conc.(%) ...	1.0	0.5	0.25	0.125
γ ...	70.70	71.45	72.21	73.10

TABLE II

Effect of temperature.

		1 % sol			2 % sol			
Temp.	...	30°	40°	50°	30°	40°	50°	60°
γ	...	70 70	70.15	69.60	67.05	65.90	64 55	63 11

TABLE III

Effect of diff. conc. of HCl *and* NaOH *on the surface tension of a 2% tannic acid sol at 30°.*

			γ.				γ.
Sol (40 c.c.)	+ 10 c.c.	water	68.27	Sol (40 c.c.)	+ 10 c c.	water	68.27
,,	+ 10	0.765 *N*-HCl	66.43	,,	+ 10	1.09*N*-NaOH	70 61
,,	+ 10	*N*/38.25 ,,	68.13	,,	+ 10	*N*/45.87 ,,	69 25
,,	+ 10	*N*/382 5 ,,	69.23	,,	+ 10	*N*/458.7 ,,	67.66
,,	+ 10	*N*/765 ,,	70.91	,,	+ 10	*N*/917.4 ,,	66.92

TABLE IV

Effect of diff. salt solns. on the surface tension of a 2% tannic acid sol at 30°.

				γ.					γ.
40 c.c.	sol. +	10 c.c.	water	68.27	40 c.c.	sol +	10 c.c.	*N*-NH_4Cl	69.40
40	,, +	,,	*N*-LiCl	67.90	40	,, +	,,	1.253 *N*-$CaCl_2$	69.23
40	,, +	,,	*N*-NaCl	69.00	40	,, +	,,	*N*-$BaCl_2$	68.90
40	,, +	,,	*N*-KCl	69.90					

TABLE V

Effect of conc. of diff. sols and temperature (of sol A) on surface tension (γ in dynes per cm.).

	γ at concentration of sol at 30°.				γ at temp. (of sol A) at		
	A.	A/2	A/4.	A/8.	40°.	50°.	60°.
V_2O_5	72.25	72.54	72.84	73.20	71.15	69.72	67.90
ZrO_2	71.85	72.42	72.95	73.55	70.55	69.11	67.93
Fe_2O_3	72.00	72.10	72.20	72.30	70.93	69.46	67.92

Vanadium Pentoxide Sol.—The sol was prepared by precipitating vanadic acid from ammonium vanadate by the action of concentrated HCl and then washing the precipitate till it had a tendency to pass to a colloidal state. The whole of the precipitate was then shaken with distilled water and the sol thus formed was allowed to dialyse till it was free from chloride ion. Dialysed sol A = 5.82 g. of V_2O_5 per litre (Table V).

Zirconium Hydroxide Sol.—The sol was prepared from Kahlbaum's sample of zirconium nitrate in the usual way and subsequently purified by dialysis. Dialysed sol A = 9.65 g. of ZrO_2 per litre (Table V).

Ferric Hydroxide Sol.—The sol was prepared by dropping ferric chloride slowly to boiling water and dialysing it. Dialysed sol A = 26.745 g. of F_2O_3 per litre (Table V).

Discussion

The results with tannic acid sol show that the greater the concentration of the sol, the higher the lowering of surface tension. The surface tension also continuously decreases with temperature and with the increasing concentration of acid. On the other hand, the surface tension increases continuously with the increasing concentration of alkali. These results are in general accord with those of gelatin and can be explained from the views already advanced and also mentioned in the beginning of this paper.

The effect of normal solutions of salts in lowering the surface tension follows the order: $Li > Na > NH_4 > K$ in the case of tannic acid.

It is probable that the solubility of tannic acid being very small, the colloidal material gives a greater number of aggregated molecules with the greater amount of acid, whilst the alkali has a tendency to simplify the colloidal particles. Adsorption being greater in the case of aggregated molecules, the lowering of surface tension is higher.

The results with the sols of vanadium pentoxide and zirconium hydroxide show that they have very little effect in lowering the surface tension of water and behave like ferric hydroxide sol although they are supposed to be hydrated (Table V).

Milner's formula (*Phil. Mag.*, 1907, *vi*, **13**, 96) connecting the surface tension of solutions and their concentrations, has been found to apply very well to the colloidal solutions of gelatin, tannic acid, etc. of various concentrations. It may be pointed out here that Johlin (*J. Biol. Chem.*, 1930, **87**, 319) believes that a relationship exists between surface tension and concentration of gelatin solution and this relationship is comparable to that obtained in solutions of surface-active substances of low molecular weight. That the collodial sols above investigated contain at least a portion of them as dissolved materials is borne out by the above consideration.

Dhar and co-workers (*Kolloid Z.*, 1927, **42**, 120) suggest that the drop in the surface tension values of lyophilic colloids is associated with their high values of viscosity and hydration. Trieschmann (*Z. physikal. Chem.*, 1935, **B29**, 328), on the

other hand, is of opinion that solvation of dissolved particles such as ions makes the inorganic salts surface-inactive.

The results show that the lowering of surface tension of water in the presence of colloidal substances is not due to high hydration and viscosity of dispersed particles but originates from the presence of a sufficient number of a dissolved polaric and aggregated molecules.

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A NEW INTERFERING AGENT IN SANCHIS' TEST FOR FLUORINE

By T. Ramakrishnan and K. Venkatramanan

The isolation and identification of a material present in a typical vegetable carbon which interferes in Sanchis' method of estimating fluorine is described.

In the course of our studies on the removal of fluorides from drinking water with paddy husk carbon, it was observed that the colour of zirconium-alizarin lake was not bleached by sodium fluoride, dissolved in tap-water, percolated through a column of paddy husk carbon. This was interpreted to mean that during the course of percolation through the carbon, the sample of water had acquired an interfering agent from the paddy husk carbon, which did not permit the reaction between the dissolved fluoride and the zirconium-alizarin lake to take place. A number of ions has been known to interfere with the reaction of dissolved fluorine with the zirconium-alizarin lake (Sanchis, *Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 134; Willard and Winter, *ibid*, 1933, **5**, 7). The permissible concentration of some of these interferring ions is given in Table I.

Table I

Ions.	Permissible conc.	Ions.	Permissible conc.
Cl'	500 p.p.m.	Ca^{++}	500 p.p.m.
SiO_3	50	Fe^{+++}	5
SO_4''	500	Mg^{++}	500
S''	2	Al^{+++}	5
HCO_3'	500	Mn^{++}	200
PO_4''	5		

In addition to the above ions, large amounts of organic matter have been known to interfere by causing precipitation of the zirconium-alizarin reagent. The sample of tap-water, which was first passed through a cation-exchange resin on the hydrogen cycle and then percolated through a column of paddy husk carbon, was analysed for the various interfering ions, and it was found that none of the ions, known to interfere with the reaction between the dissolved fluoride and the zirconium-alizarin lake, was present in a concentration higher than the permissible limit. Consequently, the unbleaching of the zirconium-alizarin lake was assumed to be due to some other interfering agent, not reported hitherto. The present communication deals with the identification of the new interfering agent.

Some Properties of the Interfering Agent.—The interfering agent is completely soluble in water, and is not volatile with steam, as it cannot be removed by filtration or by boiling.

The substance is organic in nature, as it can be destroyed by ashing the residue left after evaporating the tap-water percolated through a column of paddy husk carbon.

The interfering agent is an anion, as determined by the use of ion-exchange resins (Kenneth and William, *J. Biol. Chem.*, 1947, **9**, 19 ; Samuelson, *Z. anal. Chem.*, 1939, **116**, 328) and as indicated by the data given in Table II.

TABLE II

Fluorine added (p.p.m.).	Fluorine found (p p.m.) TW passed through C.	TW passed through C, passed through H^+ exch. (neutralised).	TW passed through C, passed through H^+ exch. and then passed through anion ex.
0.6	0.0	0.0	0.4
1.0	0.0	0.2	1.0
1.4	0 3	0.3	1.4
1 8	0.45	0.45	1.7
2.2	0.5	0.5	2.0
2.4	0.6	0.6	2.2

The small amount of interference remaining may be tentatively attributed to the incomplete removal of the anion by the exchanger, probably due to the incomplete ionisation of the anion.

The interfering agent being anion is further confirmed by the observation that it forms an insoluble salt with calcium which is soluble in dilute sulphuric acid, and is oxidisable with both acid and alkaline permanganate.

After oxidation with acid or alkaline permanganate, the substance no more behaves like an interfering agent, as shown by the data given in Table III.

To counteract the possible effect of permanganate, fluorine standards with the same amount of permanganate in tap-water were also put up side by side.

TABLE III

	Set I		Set II	
	Fluorine (p.p.m.)		Fluorine (p.p.m.)	
	added.	found.	added.	found.
Tap-water passed	0.6	0.8	0.6	0.9
through carbon	1.4	1.1	1.4	1.6
+ $CaCl_2$	2 0	1.7	2.0	1.9
Tap-water passed	0.6	0.55	0.6	0 9
through carbon	1.0	0.85	1.0	1.2
+ $KMnO_4$.	2.0	1.90	2.0	1.9

Isolation of the Interfering Agent.—Since the calcium precipitate was very small in quantity (1.5 g.) even when about 8 litres of the treated water were boiled with calcium chloride, only traces of the material were present and still capable of interfering.

Attempts were made in four different directions to examine the nature of the material and to develop tests by which its presence could be easily tested :

(1) The aqueous extract of the carbon was evaporated to dryness in the presence of a little alkali, and tests were conducted on this residue.

(2) A very dilute ($N/400$) solution of sulphuric acid, instead of the effluent from the hydrogen-ion exchanger, was percolated through the bed of carbon as the acid would be expected to extract out the interfering material more effectively.

(3) The aqueous extract was boiled with a solution of calcium chloride and tests were conducted on the precipitate formed.

(4) The aqueous extract was percolated through a cation exchanger and then through a bed of an anion exchanger. The latter bed which was found to retain most of the interfering material was eluted with a solution of alkali and tests were conducted on the residue obtained by evaporating the solution.

Identification of the Interfering Agent.—The residue in all these cases gave identical tests. It was treated with ether and the ether extract evaporated to dryness, taken up in hot water, filtered and tested for fluorine. No inhibition of bleaching was noticed. The residue from the ether extract gave reactions which pointed to the possible presence of tartaric or related hydroxy-acid. Thus, it charred with concentrated sulphuric acid; an aqueous solution gave a yellowish brown colour with ferric chloride and reduced alkaline permanganate through the green manganous stage. The absence of mirror test or ferrous test ruled out the possibility of the interfering agent being tartaric acid. The substance formed potassium and calcium salts which were insoluble in water. With resorcinol and concentrated sulphuric acid, it gave a red ring, a test for many hydroxy-acids. This test has been found the most sensitive for the interfering material and holds good even in very dilute solutions, so that it can be applied straight-away to the water treated by the carbon to see whether the interfering material is present. (When the interference is removed, as, for example, by passing the water through ion-exchange resins, no red ring is formed with these reagents.) The acid extract of the residue gave, like all α-hydroxy-acids, coloration with β-naphthol in concentrated sulphuric acid, a blue colour first formed turning to orange on dilution.

Since tartaric acid is known to be absent, another hydroxy-acid, which forms an insoluble potassium salt and may be present, is saccharic acid. Tests were made to find out if this material was the interfering agent. In fact, tests for saccharic acid like cobalt nitrate colour reaction, iodoform test and β-naphthol test were responded to by this material.

Preparation of Derivatives.—Out the elute from the anion exchanger, the phenylhydrazine derivative was prepared and crystallised from alcohol, m.p. 208° (lit. m.p. 210°). From the same elute, a dye was prepared with phenylhydrazine-*p*-sulphonic acid. It dyed silk pinkish yellow just like saccharic acid.

Interference of known Hydroxy-acids.—These tests appear to show that the interfering material is an organic hydroxy-acid and that it can be detected in solution by resorcinol or β naphthol in sulphuric acid. It was thought desirable at this stage to see whether pure simple organic acids inhibited the bleaching of zirconium lake by fluorine.

As a preliminary measure, to a solution containing different amounts of fluorine ranging from 0.6 to 2.0 p.p.m. were added 5 c.c. of 0.2% tartaric, citric, oxalic, malic and saccharic acids. These, as well as similar solutions not containing these acids, were treated with the usual Sanchis' solutions. Of these, citric, oxalic and malic acids inter-

fered in the opposite direction, giving higher values for fluorine, and hence eliminated. Tartaric acid inhibited the bleaching to some extent, while saccharic acid interfered much more, a small trace being sufficient to give a low value for fluorine. Though tartaric acid had to be eliminated in this particular case as the mirror test was not obtained, different concentartions of tartaric and saccharic acids were tried and the interference in each case determined. Finally, 100 c.c. of each of these solutions were evaporated to dryness, ignited and made up to the original volume and put up for fluorine estimation by Sanchis' method. As is shown in Table IV, in all the instances, interference was completely removed. Similarly, the solutions treated with calcium chloride and filtered off from the precipitate formed also lost the interference.

TABLE IV

Fluorine added (p.p.m.)	Fluorine found (p. p. m.) Tartaric acid (0.2%).	Ignited tartatic acid.	Saccharic acid (0.2%).	Ignited saccharic acid.	Malic acid (1.0%).	Ignited malic acid.
0.6	0.5	0.6	0.3	0.6	1.4	0.65
1.0	1.0	1.0	0.5	1.0	1.9	1.0
1.4	1.1	1.3	0.7	1.2	2.3	1.4
2.0	1.4	1.9	0.9	1.9	2.5	2.0

Confirmation of the Interfering Agent by the Paper Chromatography Method.—Thus, saccharic acid may be one of the agents chiefly responsible for the interference in Sanchis' test in water, treated by paddy husk carbon. As a confirmatory test for the organic acid, the paper chromatography method of Lugg and Overell (*Aus. J. Sci. Res.*, 1948, **1A**, 98) was used with modificactions as applied to the mixed chromatography of Giri *et al.* (*J. Ind. Inst. Sci.*, 1952, **34**, 95). A small circle of about 4 cm. diameter was drawn with a pencil from the centre of a circular filter paper. The elute from the anion exchanger (about 5μ 1) was applied all along the circumference of the circle from the tip of a capillary tube. Four such spots were placed, leaving some space between the adjoining spots where known organic acids, viz., tartaric, saccharic, malic and oxalic acids were applied. After drying, the chromatogram was developed by running a mixture of butanol-acetic acid-water mixture from the centre. Next, bromophenol blue solution (0.04% in alcohol) was sprayed on the paper, when the location of the organic acids was shown as a small concentric yellow arc against a blue background. The arc of the elute joined with that of saccharic acid alone, thus confirming the test that saccharic acid is the interfering agent.

It is therefore advisable to test for saccharic acid as an interfering agent in Sanchis' test for fluorine when vegetable carbons are used for removal of fluorine from water.

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POTASSIUM METAPERIODATE AS A VOLUMETRIC REAGENT. PART IV. IODINE CYANIDE METHOD

By Balwant Singh and Apar Singh

Potassium metaperiodate has been used as an oxidising reagent in the volumetric estimation of potassium iodide, hydrazine sulphate, stannous chloride, potassium ferrocyanide, hydrogen peroxide, arsenious oxide, tartar emetic, hydroquinone, potassium sulphocyanide, ferrous ammonium sulphate, sodium thiosulphate, sodium sulphite, sodium bisulphite, sulphurous acid, lead iodide, mercuric iodide and silver iodide by the iodine cyanide method.

Potassium metaperiodate in acid solution is a strong oxidising agent. It is reduced to iodine.

$$2IO_4^- + 16H^+ + 14e = I_2 + 8H_2O \quad \ldots \quad \ldots \quad (1)$$

The iodine is oxidised by the periodate

$$3I_2 + IO_4^- + 8H^+ = 7I^+ + 4H_2O \quad \ldots \quad \ldots \quad (2)$$

The end of the titration is reached through this reaction, whose completion is shown, in the presence of a suitable indicator (starch), by the disappearance of the free iodine. In the presence of hydrogen cyanide, the cation I^+ changes at once into stable iodine cyanide.

This method therefore is based on titration with the periodate in the presence of hydrogen cyanide, the periodate being quantitatively converted into iodine cyanide.

In presence of potassium cyanide and hydrochloric acid, potassium metaperiodate reacts in accordance with the equations :

$$KIO_4 + 3KI + 4HCl + + 4HCN = 4KCl + 4ICN + 4H_2O$$

$$2KIO_4 + 3N_2H_4 + 2HCl + 2HCN = 2KCl + 2ICN + 8H_2O + 3N_2$$

$$KIO_4 + 3SnCl_2 + 7HCl + HCN = KCl + 3SnCl_4 + ICN + 4H_2O$$

$$KIO_4 + 6K_4Fe(CN)_6 + 7HCl + HCN = 7KCl + 6K_3Fe(CN)_6 + ICN + 4H_2O$$

$$KIO_4 + 3H_2O_2 + HCl + HCN = KCl + 3O_2 + ICN + 4H_2O$$

$$2KIO_4 + 3As_2O_3 + 2HCl + 2HCN = 2KCl + 3As_2O_5 + 2ICN + 2H_2O$$

$$2KIO_4 + 3Sb_2O_3 + 2HCl + 2HCN = 2KCl + 3Sb_2O_5 + 2ICN + 2H_2O$$

$$KIO_4 + 3C_6H_4(OH)_2 + HCl + HCN = KCl + 3C_6H_4O_2 + ICN + 4H_2O$$

$$KIO_4 + KCNS = ICN + K_2SO_4$$

$$KIO_4 + 6FeSO_4 + 7HCl + HCN = KCl + 2Fe_2(SO_4)_3 + 2FeCl_3 + ICN + 4H_2O$$

$$4KIO_4 + 3Na_2S_2O_3 + 4HCN = 2K_2SO_4 + 3Na_2SO_4 + H_2O + H_2SO_4 + 4ICN$$

$$KIO_4 + 3Na_2SO_3 + 7HCl + HCN = KCl + 6NaCl + 3H_2SO_4 + ICN + H_2O.$$

$$KIO_4 + 3NaHSO_3 + 4HCl + HCN = KCl + 3NaCl + 3H_2SO_4 + ICN + H_2O$$

$$KIO_4 + 3H_2SO_3 + HCl + HCN = KCl + 3H_2SO_4 + ICN + H_2O$$

$$2KIO_4 + 3PbI_2 + 8HCl + 8HCN = 2KCl + 3PbCl_2 + 8ICN + 8H_2O$$

$$2KIO_4 + 3HgI_2 + 8\ HCl + 8HCN = 2KCl + 3HgCl_2 + 8ICN + 8H_2O$$

$$KIO_4 + 3AgI + 4HCl + 4HCN = KCl + 3AgCl + 4ICN + 4H_2O$$

EXPERIMENTAL.

Potassium metaperiodote was prepared by the method of Bahl and Singh (this *Journal*, 1940, **17**, 167).

A known weight of each substance in solution was taken in a stoppered conical flask. About 8 c. c. of 0.5*N*-KCN, at least 50 c c. of 2.5*N*-HCl, about 1 g. of sodium chloride and some starch solution were added and the titration with *M*/60-KIO_4 was carried out to the discharge of the iodine-starch blue colour, which appeared at the beginning of the titration. In these titrations normality of the solution with respect to hydrocholoric acid was maintained at about 1*N*.

All the substances, except potassium iodide, hydrazine sulphate, stannous chloride, lead iodide, mercuric iodide and silver iodide were pre-oxidised before titration. Potassium ferrocyanide and hydrogen peroxide were pre-oxidised with hypo-iodous acid (5 c. c. of 0.5*N*-ICl and 20 c. c. of 10% NaOH) in an alkaline medium and after pre-oxidation the solutions were acidified with hydrochloric acid. The rest of the substances were pre-oxidised with 5 c. c. of 0.5*N*-ICl in presence of hydrochloric acid.

In the case of sodium thiosulphate, sodium sulphite, sodium bisulphite and sulphurous acid, the titration mixture was cooled in ice-cold water and titrated rapidly against standard potassium metaperiodate until a distinct iodine-starch blue colour was imparted to the solution. The titration was then continued slowly with thorough shaking till the discharge of the blue colour. In case of titration of large quantities of these substances, their solutions were added to 10 to 15 c. c. of iodine monochloride contained in a titration flask. Iodine monochloride reacted with them quantitatively liberating iodine and thus prevented the loss of sulphur dioxide during the titration. The liberated iodine was titrated as usual against standard potassium metaperiodate solution in of presence potassium cyanide.

Lead iodide (up to 0.4 g.) was dissolved in a small amount of sodium hydroxide solution, acidified with 20 c. c. of 1:1 hydrochloric acid and titrated against standard potassium metaperiodate solution in presence of 10 to 15 c. c. of potassium cyanide and a few c. c. of starch solution.

Mercuric iodide (up to 0.4 g.) was dissolved in potassium cyanide solution, acidified with 12 c. c. of 1:1 hydrochloric acid and titrated against standard potassium metaperiodate in presence of starch solution.

Silver iodide (up to 0.4 g.) was dissolved in 10 c. c. of potassium cyanide solution and reduced at the boiling point to metallic silver with iron free zinc in presence of a little sodium hydroxide. When the reduction was complete, the suspension was filtered and the precipitate washed with water and dilute hydrochloric acid. The filtrate was acidified with 12 c. c. of concentrated hydrochloric acid and titrated against standard potassium metaperiodate solution after the addition of starch as an indicator.

Several titrations were performed in each case. From the volume of potassium metaperiodate used, corresponding to the end-point in each titration, the amount of each substance was calculated. The results are given in the following tables.

TABLE I

Potassium iodide			Hydrazine sulphate.		
$M/60$-KIO_4.	taken	found.	$M/60$-KIO_4.	taken.	found.
13.0 c c.	0.10793 g.	0.10788 g.	15 0 c.c.	0.04876 g.	0.04873 g.
22.0	0.18266	0.18257	25.0	0.08127	0.08123
50.0	0 41515	0.41499	40.1	0.13000	0.13028
	Stannous chloride.			Potassium ferrocyanide.	
	$SnCl_2.2H_2O$			$K_4Fe(CN)_6.3H_2O$	
13.50 c.c.	0.1520 g.	0.1525 g.	10 00 c.c.	0 4220 g.	0.4220 g.
24.70	0.2800	0.2791	17.00	0 7174	0.7174
33.40	0.3775	0.3775	30.85	1.3082	1.3019
	Hydrogen peroxide.			Arsenious oxide.	
16.30 c.c.	0.002774 g.	0.00277	10.00 c.c.	0.0495 g.	0.0494 g
24.40	0.00414	0.00414	27.10	0 1336	0.1341
36.80	0.00629	0.00625	43.10	0.2128	0.2133
	Tartar emetic.			Hydroquinone.	
10.10 c.c.	0.1669 g.	0.1686	10 00 c.c.	0.0550 g.	0.0550 g
25.20	0.4175	0.4208	20.00	0.1100	0.1100
37.30	0.6179	0.6229	38.00	0.2035	0.2090

TABLE II

Potassium sulphocyanide			Ferrous ammonium sulphate.		
$M/60$-KIO_4	taken.	found.	$M/60$-KIO_4.	taken.	found.
10.15 c.c.	0.01617 g.	0.01640 g.	10.65 c.c.	0.04175 g.	0.04174 g
25.00	0.04042	0.04040	21.30	0.08343	0.08349
33.10	0.05336	0.05348	30.50	0.11058	0.11056
	Sodium thiosulphate $Na_2S_2O_3, 5H_2O$			Sodium sulphite.	
10.00	0.0310 g.	0.0310 g.	15.00 c.c.	0.09451 g.	0.09451 g
23.00	0.0713	0.0713	20 00	0.12602	0.12602
37.00	0.1147	0.1147	30.00	0.18903	0.18903
	Sodium bisulphite.			Sulphurous acid.	
20.00	0.1040 g.	0.1040 g.	10.00	0.04102 g.	0.04102 g
26.00	0.1352	0.1352	21.10	0.08655	0.08655
40.10	0.2080	0.2085	33.00	0.13536	0 13536
	Lead iodide.			Mercuric iodide.	
10.00	0.1153 g.	0 1153 g.	10 00	0.1137 g.	0.1137 g.
20.10	0.2306	0.2318	23.00	0.2620	0.2615
30.10	0.3460	0.3470	30.00	0.3411	0.3411

TABLE III

AgI taken.	$M/60$-KIO_4 used.	AgI found.
0.2000 g.	17.00 c.c.	0.1997 g.
0.2820	24.00	0.2820
0.3900	33.30	0.3912

From the above results it is concluded that potassium iodide, hydrazine sulphate, stannous chloride, potassium ferrocyanide, hydrogen peroxide, arsenious oxide, tartar emetic, hydroquinone, potassium sulphocyanide, ferrous ammonium sulphate, sodium thiosulphate, sodium sulphite, sodium bisulphite, sulphurous acid, lead iodide, mercuric iodide and silver iodide can be determined quantitatively by the iodine cyanide method, using potassium metaperiodate as a volumetric reagent.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART XIII. OXIDATION WITH POTASSIUM METAPERIODATE

By Balwant Singh, Apar Singh and Roshan Singh

Mercurous chloride, stannous chloride, arsenious oxide, tartar emetic, hydrazine hydrochloride and potassium sulphocyanide have been estimated by a potentiometric method, using potassium metaperiodate as an oxidising agent.

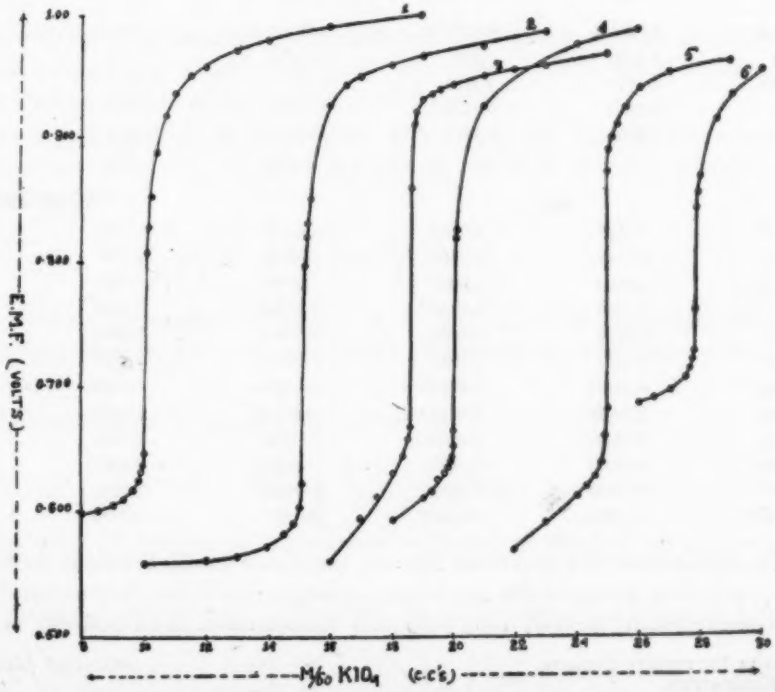
Singh and Singh (this *Journal*, 1952, **29**, 34) have shown that potassium metaperiodate reacts with mercurous chloride, stannous chloride, arsenious oxide, tartar emetic, hydrazine hydrochloride and potassium sulphocyanide in presence of concentrated hydrochloric acid.

The reactions have been utilised in the quantitative determination of these substances by the potentiometric method using potassium metaperiodate as an oxidising agent.

Experimental

Potassium metaperiodate was prepared by the method of Bahl and Singh (*ibid.*, 1940, **17**, 167).

Fig 1.



Curves 1-6 refer respectively to NH_2. NH_2.HCl, KCNS, $SnCl_2$, Hg_2Cl_2, As_2O_3 and tartar emetic

The oxidation-reduction electrode, which consisted of a bright platinum foil immersed in a solution to be titrated, was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. The cell was placed in a water-bath, the temperature of which was maintained at 20°. E.M.F. of the cell was read on a potentiometer.

A known weight of each substance was mixed with water, acidified with concentrated hydrochloric acid and titrated against standard potassium metaperiodate. In these titrations, normality of the solution with respect to hydrochloric acid was kept between $4N$ and $7N$. The titrations were conducted in an atmosphere of carbon dioxide and the mixture was kept stirred by a mechanical stirrer.

The titrations, one for each subtance, are represented by the curves given in Fig. 1.

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in the potential, followed by a steady rise in each case.

From the amount of potassium metaperiodate used, corresponding to equivalence point in each titration, the amount of each substance was calculated. In the following table the values obtained are compared with the amounts of the substances taken.

TABLE I

KIO_4 used.	Hg_2Cl_2.		KIO_4.	$SnCl_2$	
	taken.	found.	used.	taken.	found.
0.0384 g.	0.2365 g.	0.2369 g.	0.07149 g.	0.2124 g.	0.2107 g.
0.0574	0.3548	0.3541	0.08962	0.2656	0.2642
0.0767	0.4730	0.4735	0.10300	0.3057	0 3037
0.0950	0.5913	0.5919	0 11895	0.3531	0.3507
0.1152	0.7095	0.7101	0.14210	0.4215	0 4184
			0.15575	0.4621	0.4591
	As_2O_3			Tartar emetic.	
0.04198	0.0545	0.0542	0.04450	0.1941	0.1939
0.05731	0.0743	0.0740	0.05931	0.2586	0.2584
0.07678	0.0990	0.0991	0.06820	0.2975	0.2971
0.09564	0.1238	0.1236	0.07998	0.3488	0.3484
0.11492	0.1485	0.1484	0.08907	0.3883	0.3880
0.15311	0.1980	0.1977	0.09781	0.4259	0.4261
0.03845	0.01713	0.01718	0.03290	0.0139	0.0139
0.05762	0.02569	0.02573	0.04350	0.0185	0.0184
0.07659	0.03425	0.03422	0.05456	0.0231	0.0230
0.09564	0.04281	0.04273	0.07112	0.0301	0.0300
0.11481	0.05138	0.05129	0.09353	0.0393	0.0395
0.13398	0.05994	0.05985	0.1150	0.0486	0.0485

The results show that mercurous chloride, stannous chloride, arsenious oxide, tartar emetic, hydrazine hydrochloride and potassium sulphocyanide can be determined directly by the potentiometric method, using potassium metaperiodate as an oxidising agent.

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SUPERSATURATION COEFFICIENT AND THE DIFFERENTIAL HEAT OF SOLUTION

By B. S. Srikantan and C. N. Venkatachallum

An equation has been derived for the calculation of heat of solution of saturated solutions from supersaturation coefficient and limits of supersaturation. The values for KCl, NH_4Cl, KNO_3 and $KClO_4$ agree with those calculated from Williamson's equation.

It has been shown by Srikantan and Ramachandra (this *Journal*, 1951, **28**, 585) that vant Hoff's isochore could be used to calculate the heat of solution of saturated solutions of substances whose temperature coefficient of solubility is constant; but for substances like NH_4Cl, $KClO_4$ and KNO_3, whose temperature coefficient of solubility is not constant, the equation becomes inapplicable. Ostwald-Freundlich equation (*Z. physikal. Chem.*, 1900, **34**, 495; "Kapillarchemie", Leipzig, 1909, p. 144) for supersaturated solution can be rewritten as

$$T_s\left(\frac{S-S_n}{S_n}\right) = \left(\frac{2M\sigma}{Rd\tau}\right) \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where $(S-S_n/S_n)$ is the supersaturation coefficient, S_n is the solubility at temperature T_s (abs.), M is the molecular weight of the solute, d is density, r is the size of solute particle and σ is the free surface energy of solute particles at T.

Jones and Partington's equation (*Phil. Mag.*, 1945, **29**, 35) for supercooling for spontaneous crystallisation, when the amount of dissolved solute is constant, gives the following relation

$$\lambda\left(\frac{T_s - T_c}{T_s}\right) = \frac{2M\sigma}{d\tau} \quad \ldots \quad \ldots \quad (2)$$

where λ is the heat of saturated solution in cal./g. mol., T_s is the temperature of saturation in degrees absolute, T_c is the temperature of spontaneous crystallisation on cooling a saturated solution.

Combining (1) and (2) one gets the relation

$$\lambda = RT_s^2\left(\frac{S-S_n}{S_n}\right) \times \frac{1}{(T_s - T_c)} \quad \ldots \quad \ldots \quad (3)$$

connecting heat of solution and supersaturation coefficient and the limit of supersaturation.

Williamson (*Trans. Faraday Soc.*, 1944, **40**, 435) proposed the following equation

$$\Delta_{Sat.}\,(H_{soln.}) = RT^2\left(\frac{dm}{dt}\right)_{ss} \times \left(\frac{1}{m}\right)_{sat} \quad \ldots \quad \ldots \quad (4)$$

where ΔH is the heat of solution of saturated solution at T and dm is the small change in concentration of saturated solution for a small change of temperature dt and m is the concentration of the saturated solution at T. The following table gives the data calculated by equations (3) and (4) for KCl, NH_4Cl, KNO_3 and $KClO_4$.

λ cal./g. is the heat of solution calculated by equation (3). The values of supersolubility coefficient $S-S_n/S_n$ are taken from a previous paper of the authors (this *Journal*, 1952, **29**, 608) and T_s-T_c are from the data of one of us (this *Journal*, 1950, **27**, 627) the relevant values being adopted for different regions. ΔH cal./g. mol. is the heat of solution calculated by equation (4); dt is taken as 10°, being 5° on either side of T, and dm, the change in solubility and m is the average solubility in that interval. The solubility data from International Critical Tables (Vol. V, p. 169) have been used.

TABLE I

Temp.	$S-S_n/S_n$.	λ cal./g. mol.	ΔH cal./g. mol.
	1. KCl. $T_s-T_c=13.1$		
30°	0.1038	1440	1440
40°	0.0921	1400	1360
45°	0.0877	1350	1340
	2. KNO_3. $T_s-T_c=3.9$ till 40° and 7.8 from 40° to 70°.		
20°	0.1591	6920	6620
50°	0.2253	5970	5750
60°	0.2011	5770	5380
	3. NH_4Cl. $T_s-T_c=3.7$ between 10° and 40° &=5.3 between 50° and 60°.		
20°	0.0459	2210	1900
30°	0.0450	2210	1950
55°	0.0434	1940	1840
	4. $KClO_4$. $T_s-T_c=6.2$ till 20° and 2.6 above 20°.		
10°	0.3109	7950	7020
30°	0.1098	7670	6860
40°	0.0896	6900	6440
50°	0.0825	6610	7350

The values of λ, heat of saturated solution, by the present equation at different temperatures agree with those of ΔH obtained from Williamson's equation. In both the equations the activity factor has not been introduced. The interionic attraction in supersaturated solutions will be greater than that for saturated solutions.

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EFFECT OF METALLIC SOAPS ON POLYMERISATION

By Jyotirindra Nath Sen and Santi R. Palit

Effect of a few oil-soluble, surface-active agents and the oleates of Cr, Ag, Cd, Pb, Cu on the benzoyl peroxide catalysed polymerisation of styrene in solution and that of the soaps of Mn, Zn, Cd, Co, Ni, Al, Fe etc. on the polymerisation of methyl methacrylate and styrene in absence of peroxide catalyst have been studied. In the former case aerosol and Cu oleate retarded, and cetavlon inhibited polymerisation. Other soaps studied showed only a very slight retarding effect.

In the uncatalysed polymerisation of methyl methacrylate Mn oleate inhibited and Zn oleate and Cd oleate retarded polymerisation, all other soaps catalysed it. With styrene all soaps excepting that of manganese, which inhibited polymerisation, showed definite catalytic activity.

In continuation of our previous work (this *Journal*, 1949, **26**, 385) we carried out a number of experiments with various metallic soaps and oil-soluble, surface-active agents on polymerisation as a preliminary survey of the whole field. As we now intend to limit ourselves to a closer study of only one or two systems from this survey, which seems to us of immediate interest with regard to the fundamentals of polymerisation kinetics, we record only the general results obtained.

Experimental

The experimental method and technique were the same as previously reported (*loc.cit.*). Viscosity measurements were carried out in benzene solution at 35° with the help of two Ostwald type viscometers of flow time 180 and 230 sec. respectively. Intrinsic viscosity (η) was obtained by extrapolating η_{sp}/c *vs.* c to zero concentration ($\eta_{sp} = \eta_s/\eta_0 - 1$) $= t_s/t_0 - 1$, where η_s and η_0 are the viscosities and t_s and t_0, the times of flow of the solution and the solvent respectively, and c is the concentration expressed in g./100 ml. solvent.

Table I

Polymerisation of 1.15 M styrene in benzene with 0.96% benzoyl peroxide and various additives at 80°.

Time = 4 hours.

Additive.	Conc. of additive (g./100 c.c soln).	Yield.	Remarks.	Additive.	Conc of additive (g./100 c.c. soln).	Yield.	Remarks
None	Nil	20.17%					V. S effective
Chromium oleate	1.12	20.05	Not effective	Leda oleate	3.4	19.2%	Do
				Triton N-100	3.2	19 1	Small retardation
Silver oleate	0.013	19.9	,,	Aerosol O.S	2.0	17.6	Retardation
Cadmium oleate	1.5	19.7	Very slight effective	Copper oleate	0.01	11.9	Strong retardation
Glycerine mono	1.3	19.6	,,	Coper oleate	2.0	0.96	Inhibition
sterate			,,	Cetavlon	2.6	0.0	

Discussion

Polymerisation in presence of Catalyst.—The results of benzoyl peroxide catalysed polymerisation of styrene (1.15 *M*) in benzene at 80° with different additives are presented in Table I. The results show that for a period of polymerisation of 4 hours and a yield of 20.17% in the reaction where no additive has been added (control experiment), cetavlon totally inhibits polymerisation, and copper oleate (2 g. per 100 c.c. solution) produces only 1.0% yield for the same period of 4 hours *i. e.* it behaves as a strong retarder of polymerisation. Effectiveness of copper oleate as a retarder is found to diminish, as expected, with decrease in its concentration. Chromium oleate and silver oleate practically exert no influence on polymerisation ; cadmium oleate, lead oleate, glycerol monostearate and triton N-100 have a very small retarding effect. Though small, the tendency to retard polymerisation by the above mentioned additives seems real and the lack of any pronounced retarding effect may partly be due to the presence of rather a high concentration of benzoyl peroxide catalyst which would mask the effects produced by the additives in such a dilute solution of the monomer. Aerosol O.S., however, retards polymerisation and produces a yield of 17.6% after 4 hours.

We, however, realised that in order to assess the true effect of these additives it would be better to work in systems without peroxide, and hence in all our later experiments we studied the effect of additives in uncatalysed polymerisation. The results are reported in the next section.

It is, however, remarkable that cetavlon is capable of completely inhibiting polymerisation against high peroxide concentration and high temperature. This contrasts strongly with the behaviour of the same substance in a reduction-activation aqueous system where even trace quantities have been found by Baxendale, Evans and Kilham (*Trans. Faraday Soc.*, 1946, **42**, 668) to stongly catalyse polymerisation. It is suggested that cetavlon or similar substances be used as commercial inhibitors offering the advantage of complete removal of the monomer by distillation.

Polymerisation in absence of Peroxide Catalyst : Styrene.—As only a few soaps are soluble in pure styrene, we have studied polymerisation of 4.6 molar solution of styrene in benzene, in which solvent soaps of magnesium, zinc, nickel, cobalt and manganese are freely soluble. The results of these experiments are shown in Table II and graphically represented in Fig. 1.

All the metallic soaps we have studied are found to catalyse the polymerisation of styrene though of course their catalytic power, as indicated by the initial slopes of the yield-time curves, vary for the different soaps. For, approximately, the same concentration of the soaps the relative effectiveness of the different metallic soaps as catalysts for styrene polymerisation follows the order: zinc oleate, magnesium oleate, cobalt oleates, nickel oleate, ferric stearate, ferric oleate.

It should be pointed out here that some of the soaps, like nickel and cobalt oleates, which were found to retard the polymerisation of 1.15% molar styrene in benzene in presence of 0.96% benzoyl peroxide (Sen, Sen Gupta and Palit, this *Journal*, 1949, **26**, 385) actually catalysed polymerisation in this case, *i.e.*, in the absence of benzoyl peroxide.

TABLE II

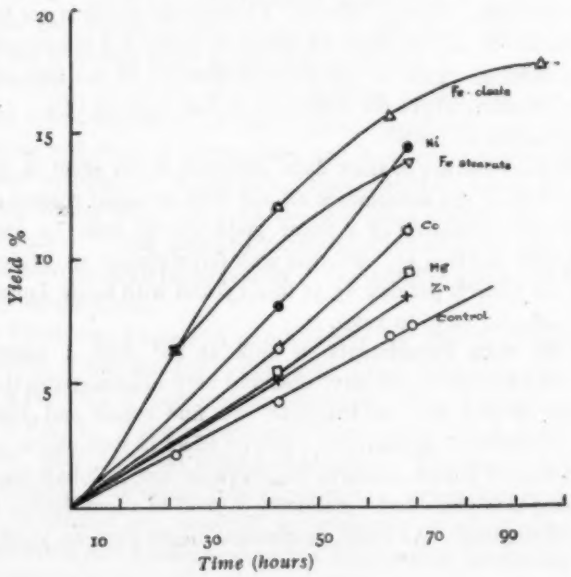
Polymerisation of 6.48M styrene in benzene at 60.4° in presence of additives.

Additive	Conc. of additive (mole/mole monomer).	Time.	% Yield.		D.P.*
None	Nil	21.5 hrs.	2.11	3.85	17,420
		42.0	4.20		
		64.5	6.85		
		69.0	7.27		
Manganese oleate	2.497×10^{-4}	42.0	0.00	—	
Zinc oleate	2.517×10^{-4}	42.0	5.05	—	
		68.0	8.38		
Magnesium oleate	2.523×10^{-4}	42.0	5.32	3.19	13,450
		68.0	9.40		
Cabalt oleate	3.321×10^{-4}	42.0	6.38	2.94	11,980
		68.0	11.08		
Nickel oleate	2.505×10^{-4}	42.0	8.02	2.92	11,900
		68.0	14.40		
Ferric stearate	2.512×10^{-4}	21.5	6.36	2.82	11,330
		68.0	13.80		
Ferric oleate	2.350×10^{-4}	21.5	6.25	1.85	6,301
		42.0	12.00		
		64.5	15.62		
		95.0	17.7		

* Calculated from equation $K_m M^a$, $K_m = 1.2 \times 10^{-4}$, $a = 0.72$
(D'Alelio, "Experimental Plastics and Synthetic Resins", p.71, John Wiley and Sons, Inc., 1946)

FIG 1.

Temp. 60.4°; styrene (6.48 mol./litre)



The retardation in the peroxide-catalysed polymerisation is possibly due to some wastage of peroxide by interaction with the metallic soaps or other complicating factors. Manganese oleate inhibits polymerisation totally. The behaviour of ferric oleate and ferric stearate as a good catalyst is maintained here. From the curves it appears that at the initial stage the rates of polymerisation with the two ferric soaps are practically the same.

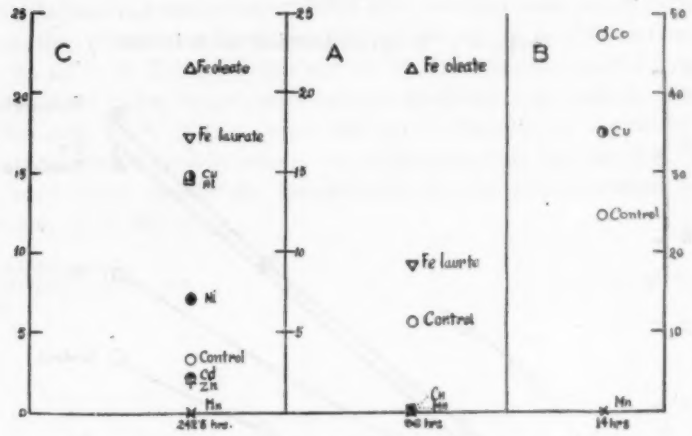
Polymerisation in absence of Peroxide Catalyst : Methyl Methacrylate: Comparative Yields.—Three series of polymerisation experiments were conducted with methyl methacrylate with the addition of a small proportion (2.4 mols. per 10,000 mols. monomer) of an added metallic soap and the extent of polymerisation was measured after a convenient interval for each series. Two of these were methyl methacrylate in bulk, one at 35° and the other at 80°. As most of the metallic soaps were found to dissolve in the monomer only with great difficulty or not at all, another series of experiments was run at 35° with the monomer diluted with an equal volume of benzene to impart solubility to a large number of soaps, thus making their examination possible. The results are graphically represented in Fig. 2.

Referring to Fig. 2A it will be observed that at as low a concentration as 2.4 mols. metallic soaps per 10,000 mols. of monomer, cobalt and iron strongly accelearate polymerisation, whereas copper and manganese pratically stop the reaction. By the time the thermal reaction (control) gives a yield of only 5%, iron oleate produces a yield of over 21% and the acceleration by cobalt oleate is so strong that the whole tube sets to a solid mass much earlier than the time allowed for the reaction. The polymer obtained with cobalt was found to swell but not to dissolve in benzene even on keeping in contact with the solvent for several days, and hence, the exact value of the yield of the polymer could not be ascertained. It is rather strange that this catalyst can produce a polymer which is insoluble in such a good solvent, a behaviour which is not known to occur with peroxide catalysts. It will be observed that iron oleate is a somewhat less powerful catalyst than iron laurate. This is further corroborated by our data at the same temperature in benzene solution, where the difference is less marked (Fig. 2, C). However, at 80° this difference seems to vanish.

The least understood feature of these data, however, is the effect of dilution on the catalysed reaction. When the monomer is diluted with an equal volume of benzene , the yield, calculated on the assumption of a linear yield curve, falls by about four times from 1.42 yield % per day to 0.33, whereas with ferric oleate as catalyst, dilution has a smaller effect on the yield% per day (5.35 to 2.13) and with ferric laurate the yield % per day is still less affected (2.56 to 1.69).

On repeating the same experiments in bulk at 80° with a conversion of about 4 times in the control experiment, we have observed very unexpectedly that the picture is completely changed (Fig. 2, B). In this case, we find cobalt and iron oleate to have fairly strong catalytic effects. In fact, the catalytic effect of iron oleate is very strong, almost as strong as that of cobalt oleate in the previous case. Cobalt oleate in this case also has a very strong catalytic effect producing a yield of about double the amount produced in the control reaction. As usual, manganese oleate gave no yield, thus behaving as an inhibitor.

FIG 2



Conc. of catalyst in all runs is 2.42×10^{-4} mols./litre.

A—Temp. 35°; methylmethacrylate (bulk) (Co oleate sets to a hard insoluble polymer).
B—Temp. 80°; Do
C—Temp 35°; Do (1 :1 by vol, in benzene)
(Fe oleate and laurate set into a hard insoluble polymer).

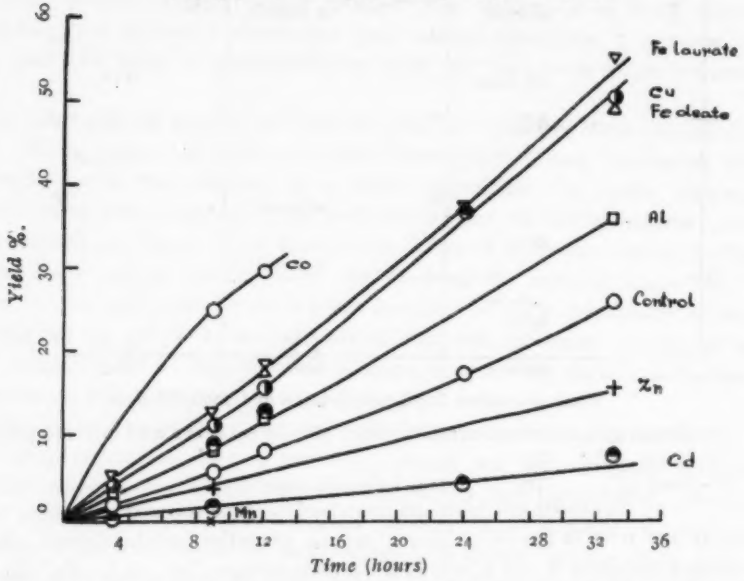
Copper in any form is known to have a strong retarding or inhibitory effect, and we have verified the same in our pervious work with styrene (*loc. cit.*). In the present study with uncatalysed methyl methacrylate polymerisation, diluted with an equal volume of benzene we unexpectedly observe copper oleate to have a small catalytic effect. We have confirmed by repeated experiments that this capricious behaviour of copper is a real one and is not due to any experimental uncertainty. Indeed, the results presented herein show that the retarding effect of copper is decreased giving place of acceleration by dilution of the monomer or by a rise of temperature.

Referring to Fig. 2,C for 1:1 monomer-benzene mixture, it may be observed that at 35°, out of the seven soaps studied iron, copper, aluminium and nickel act as catalysts, whereas cadmium and zinc act as retarders, and manganese as an inhibitor. The behaviour of iron and manganese is somewhat similar to their action on bulk polymerisation at the same temperature (Fig. 2,A). Of the new soaps studied that of aluminium behaves as a strong catalyst. This powerful catalytic effect of aluminium soap perhaps undisputedly proves that the catalytic behaviour of the metallic soaps has nothing to do with variable valency of the metal.

Complete Yield-time Curve.—A rough survey of the field being obtained in the above experiments, it was decided to determine a full yield-time curve for all the metallic soaps to have a fair idea of their relative efficiency. This has been done and the results are presented in Fig. 3. These experiments were performed at 80° with methyl methacrylate, diluted with an equal volume of benzene. The results in the main corroborate our foregoing findings with single tube experiments. It is further seen that no spurious effect due to impurities are involved, as otherwise it would not have been possible to obtain such consistent data throughout such a long period, producing a high conversion. It is observed that manganese behaves as an inhibitor, and that zinc and cadmium are retar-

FIG 3.

Temp., 80°. Methyl methacrylate (4.6 mol./litre)



ders, whereas aluminium, nickel, iron, copper and cobalt are all strong catalysts for polymerisation under the experimental conditions. Cobalt, as previously observed, has got the strongest effect producing nearly 4 times more yield of the polymer than in the control experiment. Next to cobalt comes iron oleate and laurate, whose curves are practically the same. Aluminium and nickel come next. The effect of zinc and cadmium seem to be those of pure retarding effects without showing any period of inhibition, whereas manganese definitely shows a rather long period of inhibition. The inhibition of manganese is very unexpected as both cobalt and manganese soaps are known to be powerful accelerators for polymerisation of drying oils, and it is difficult to see by what mechanism this inhibition is produced.

The effect of temperature and dilution is worth noting. If we suppose that the thermal polymerisation, and that initiated by metallic soaps are quite independent of each other, and if we assume for rough calculation that the yield is roughly proportional to time, we can easily observe from Fig. 2c and Fig. 3 that a rise of temperature of 45° (from 35° to 80°) increases the speed of the iron laurate or oleate catalysed reaction barely 20 times or less. In other words, polymerisation initiated by metal soaps is less sensitive to temperature than thermal polymerisation. We have already pointed out a diminished sensitivity of the speed of the former reaction to dilution with benzene as compared to the purely thermal polymerisation. Of course, the above conclusions are based on the concept that the thermal and the catalysed polymerisation are concurrent independent reactions which, however, is yet to be proved.

Measurement of molecular wieght or degree of polymerisation of the products obtained in catalysed and control experiments have not been made in a systematic manner. Nevertheless, the values of intrinsic viscosity and degree of polymerisation, calculated therefrom, as given in Table II, show that the D. P. of samples produced in the control experiment is much higher than those of samples produced in the metallic soap catalysed reaction (Sen and Palit, *Nature*, 1950, **166**, 603). Though this is quite in conformity with our expectations, it must be pointed out at the same time that the D.P. is never so low (*ca.* 1000) as to justify the assumptions of polar polymerisation (Heiligmann, *J. Polymer Sci.*, 1944, **66**, 1594).

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COMPOSITION OF URANYL FERRO AND FERRICYANIDES BY PHYSICO-CHEMICAL METHODS. PART I. CONDUCTOMETRIC STUDIES ON THE COMPOSITION OF URANYL FERROCYANIDE

By Jagdish N. Gaur, H. C. Gaur and Abani K. Bhattacharya

The composition of uranyl ferrocyanide has been studied by conductometric titrations of uranyl nitrate and potassium ferrocyanide at several concentrations in aqueous and aqueous alcoholic solutions. The compositions obtained both by direct and reverse titrations are analogous, and the equivalence points both in the direct and reverse titrations indicate the formation of the compound $K_2(UO_2)Fe(CN)_6$, $xUO_2(NO_3)_2$ which, in all probability, are adsorption complexes.

There is hardly any reference in the literature on the study of the uranyl ferrocyanide by physico-chemical methods. Atanasiu (*Bul. Soc. romona, Sttiinte*, 1928, **30**, 69) investigated the composition of uranyl ferrocyanide by potentiometry, but his conclusions were undecisive. Due to high adsorptive property of uranyl ferrocyanide, and also due to its hydrolysable character, analytical methods have not so far afforded any conclusive results.

Physico-chemical methods have, by far, given more conclusive evidences for the composition of many insoluble ferro- and ferricyanides (Bhattacharya and Gaur, this *Journal*, 1947, **24**, 487, 499; 1948, **25**, 27, et seq.). In this paper the results obtained by conductometric titrations are communicated and the nature of the composition of uranium ferrocyanide obtained from the equivalence points has been discussed.

Experimental

Analar (B.D.H.) reagents were used. Preparation of standard solutions and further dilutions were done with conductivity water. Potassium ferrocyanide solution was estimated as described in a previous publication (this *Journal*, 1951, **28**, 473). Uranium in uranyl nitrate solution was estimated as U_3O_8 by evaporating 25 c.c. of the prepared (A/2) solution, in a platinum crucible, on a water-bath and heating the residue in full flame of a Mecker burner until the weight of the precipitate was constant. The measurements of conductance were done by Kohlrausch's universal Bridge (W. G. Pye). As a source of A. C., a low frequency oscillator (1000 c/s. Philiphs type 4260/1, No. RT-167) was used, the point of balance being indicated by a minimum of sound in the headphone. The conductivity cell was of Arrhenius type and during the course of titration it was kept immersed in a thermostat maintained at room temperature (31°). The titrations were carried out by taking 10 c.c. of one of the reactants in the conductivity cell while the other was added gradually from the burette. The conductance of the solution after each addition was measured and was corrected for dilution effect by multiplying the observed conductance by v/10, where v was the total volume of the solution and 10 c.c. referred to the volume of the reactant taken in the cell (Davies, "The Conductivity of Solutions", p.238). Curves were plotted between the corrected

TABLE I

Direct titrations.

Theoretical value : 10 c.c. of $M/4.855$ $K_4FeCy_6 \equiv 10.117$ c.c. of $M/4.912$ $UO_2(NO_3)_2$.

A/10-K_4FeCy_6 in the cell (v c.c.)	Alcohol added.	$UO_2(NO_3)_2$ required for v c.c. of A/10 K_4FeCy_6 (v_1).	$UO_2(NO_3)_2$ calc. for 10 c.c. of A/10-K_4FeCy_6 [$(v_1/v)10$].	Equiv. vol. of A/10-$UO_2(NO_3)_2$ [$n(v_1/v(10)$.	Compound formed.	Curve
	A/1-$UO_2(NO_3)_2$ added to A/10-K_4FeCy_6.			Conc. ratio (n) = 10 : 1.		
10 c c.	0 c.c.	1.16	1.16	11.6	$K_2(UO_2)FeCy_6$, $0.146UO_2(NO_3)_2$	1
9	1	1.00	1.11	11.1	$K_2(UO_2)FeCy_6$, $0.097UO_2(NO_3)_2$	2
8	2	0.88	1.10	11.0	$K_2(UO_2)FeCy_6$, $0.087UO_2(NO_3)_2$	3
	A/2-$UO_2(NO_3)_2$ added to A/10-K_4FeCy_6.			Conc. ratio (n) = 5 : 1.		
10 c.c.	0 c.c.	2.3	2.3	11.5	$K_2(UO_2)FeCy_6$, $0.136UO_2(NO_3)_2$	4
9	1	2.0	2.22	11.1	$K_2(UO_2)FeCy_6$, $0.097UO_2(NO_3)_2$	5
8	2	1.76	2.20	11.0	$K_2(UO_2)FeCy_6$, $0.087UO_2(NO_3)_2$	9

TABLE II

Reverse titrations.

Theoretical value : 9.88 c.c. of $M/4.855$ $K_4FeCy_6 \equiv 10$ c.c. of $M/4.912 UO_2(NO_3)_2$.

A/10-$UO_2(NO_3)_2$ in the cell (v c.c.)	Alcohol added.	K_4FeCy_6 reqd. for v c.c. of $UO_2(NO_3)_2$ (v_1).	K_4FeCy_6 calc. for 10 c.c. of $UO_2(NO_3)_2$ [10 (v_1/v)].	Equiv. vol of A/10-K_4FeCy_6 [n (v_1/v) 10].	Compound formed.	Curve.
	A/1-K_4FeCy_6 added to A/10-$UO_2(NO_3)_2$.			Conc. ratio (n) = 10 : 1.		
10 c.c.	0 c.c.	0.83	0.83	8.3	$K_2(UO_2)FeCy_6$, $0.190UO_2(NO_3)_2$	1
9	1	0.76	0.84	8.4	$K_2(UO_2)FeCy_6$, $0.176UO_2(NO_3)_2$	2
8	2	0.68	0.85	8.5	$K_2(UO_2)FeCy_6$. $0.162UO_2(NO_3)_2$	3
	A/2-K_4FeCy_6 added to A/10-$UO_2(NO_3)_2$.			Conc. ratio (n) = 5 : 1.		
10 c.c.	0 c.c.	1.68	1.68	8.4	$K_2(UO_2)FeCy_6$, $0.176UO_2(NO_3)_2$	4
9	1	1.56	1.73	8.65	$K_2(UO_2)FeCy_6$, $0.142UO_2(NO_3)_2$	5
8	2	1.40	1.75	8.75	$K_2(UO_2)FeCy_6$, $0.129UO_2(NO_3)_2$	6

conductance thus obtained against the volume of the reactant. The breaks in the curves correspond to the formation of the different complexes. Using different concentrations of the two salt solutions, titrations were performed by direct and reverse methods, *i.e.* when uranyl nitrate from the burette was added to potassium ferrocyanide in the cell and *vice versa*. Titrations were done in the presence of alcohol up to 20% by volume. A/1 potassium ferrocyanide solution corresponds to $M/4.855$ and A/1 uranyl nitrate solution corresponds to $M/4.912$.

The results of the conductometric titrations have been summarised in Tables I and II.

Discussion.

From column five in the above tables it will be seen that in direct titrations the volume of uranyl nitrate required for 10 c.c. of potassium ferrocyanide is slightly more than that required for the formation of the compound in the molar ratio of 1:1. The discrepancy between the calculated and observed titre values gradually reduces by increasing the amount of alcohol in aqueous alcoholic solutions. The molecular composition of uranyl ferrocyanide obtained from the equivalence points both in the direct and reverse titrations corresponds to the compound $K_2UO_2FeCy_6$, $x\ UO_2(NO_3)_2$ where x varies slightly with the concentration ratio of the reactants. The value of x also varies with the quantity of alcohol added to the solution taken in the beaker. These observations suggest that the higher value of uranyl nitrate than the calculated one in direct titration, and lower value of potassium ferrocyanide in the reverse titrations result from the selective adsorption of uranyl nitrate by the precipitate of uranyl ferrocyanide.

In the direct titration the reaction takes place in the medium of potassium ferrocyanide, and hence, an adsorption compound with potassium ferrocyanide can be anticipated, but the result of the titration shows that the precipitated complex takes more uranyl nitrate at the equivalence point which results in the formation of an adsorption compound with uranyl nitrate. This seems to be due to much greater adsorption of uranyl nitrate than potassium ferrocyanide by the precipitated complex. The hydrolysis of uranyl ferrocyanide may also be responsible for a similar result according to the equation

$$K_2UO_2FeCy_6 + 2\ H_2O = K_2H_2FeCy_6 + UO_2(OH)_2$$

The hydrolysed product $K_2H_2FeCy_6$ may now combine with more of uranyl nitrate than the equivalent amount resulting in the formation of a complex of the type $K_2(UO_2)FeCy_6$, $xUO_2(NO_3)_2$, the value of x depending upon the degree of hydrolysis of the precipitated complex.

In the reverse titration also the formation of an analogous compound can be explained. In this case a greater adsorption of uranyl nitrate can be anticipated since the reaction takes place in the medium of uranyl nitrate. The hydrolysis of K_2UO_2-$FeCy_6$ can also bring about the formation of similar complexes, because uranyl nitarte will be partly used up by the hydrolysed product $K_2H_2FeCy_6$ during the course of the reaction, and hence, the titre value of potassium ferrocyanide at the equivalence point will be much less than the theoretical amount.

FIG. 1 (curve 1)

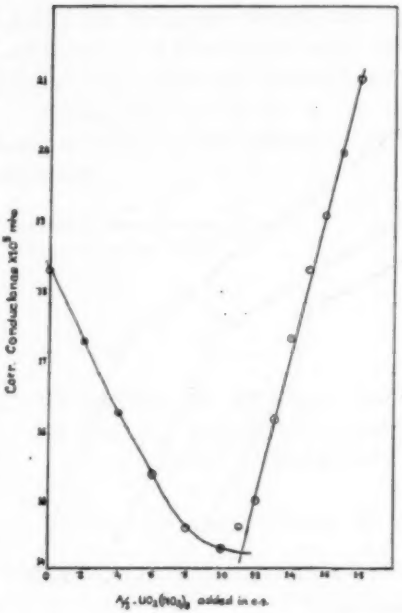


FIG. 2 (curves 2 and 3)

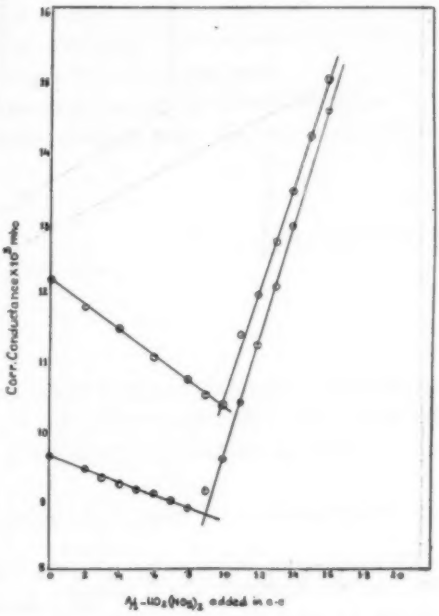


FIG. 3

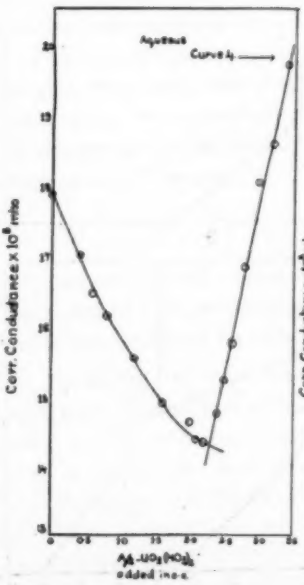


FIG. 4

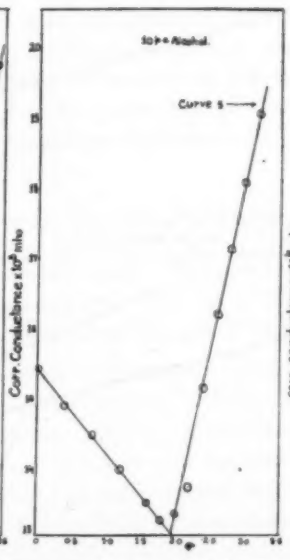


FIG. 5

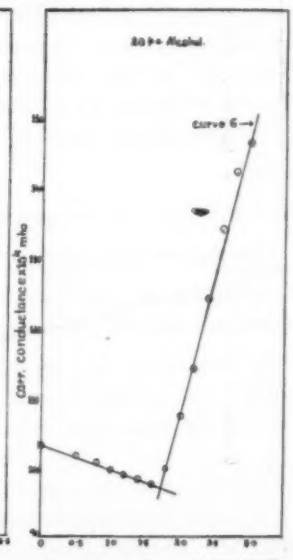


FIG. 6

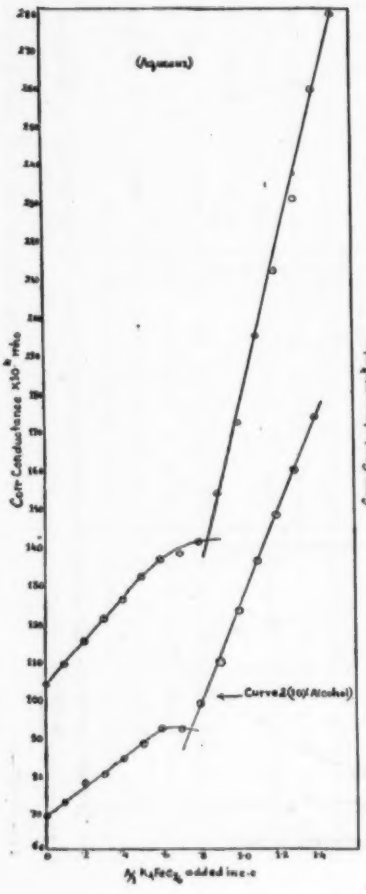


FIG. 7

Reverse titrations

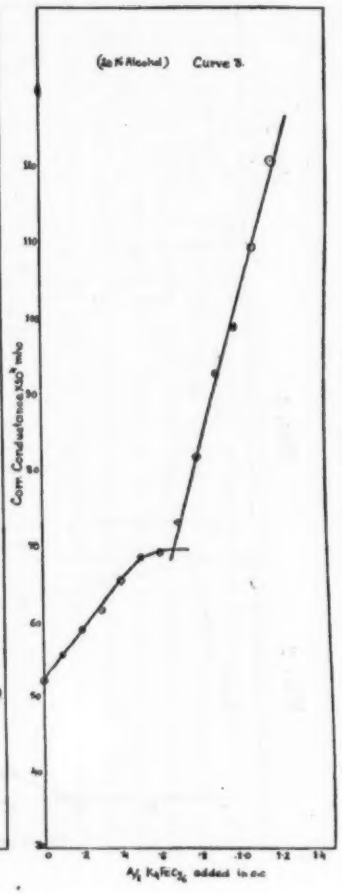
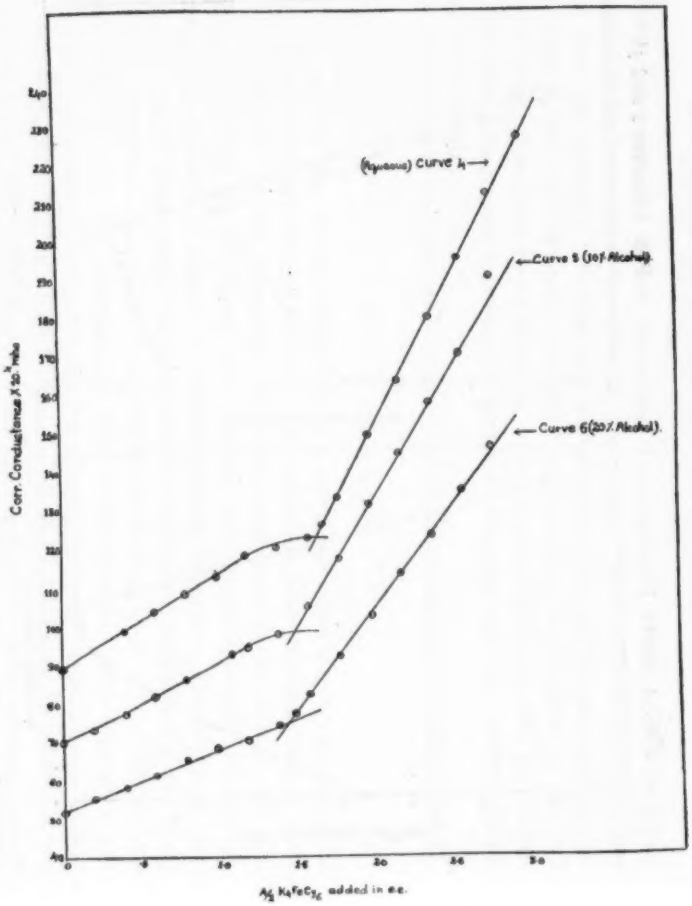


FIG. 8



It is difficult to allocate the proportional contribution of adsorption and hydrolysis towards the formation of such compounds as have been observed, viz., $K_2UO_2FeCy_6$, $x\ UO_2(NO_3)_2$. Experimental work on the hydrolysis and adsorption of uranyl ferrocyanide is in progres and the results will form a later communication.

Thanks are due to Dr. S. S. Deshapande for kindly permitting one of us (J. N. Gaur) to work in the laboratory of Agra College, who did the experimental part elaborately.

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COMPOSITION OF URANYL FERRO AND FERRICYANIDES BY PHYSICO-CHEMICAL METHODS. PART II. POTENTIOMETRIC STUDIES ON THE COMPOSITION OF URANYL FERROCYANIDE

BY JAGDISH N. GAUR, H. C. GAUR AND ABANI K. BHATTACHARYA

The composition of uranyl ferrocyanide has been studied by potentiometric titration of uranyl nitrate and potassium ferrocyanide at several concentrations in aqueous and aq. alcoholic solutions. The composition of uranyl ferrocyanide indicated by the equivalence points corresponds to the type $K_2(UO_2)FeCy_6$, $xUO_2(NO_3)_2$. There is a good agreement between the observations by potentiometry and conductometry.

In continuation of our observations on conductometric titrations between uranyl nitrate and potassium ferrocyanide (this *issue*, p.158) potentiometric titrations were carried out between the same reactants. Atanasiu (*Bull. Soc. romana, Sttiinte*, 1928, **30**, 69) investigated the composition of uranyl ferrocyanide by potentiometry but his conclusions were undecisive. Our observation on the composition of uranyl ferrocyanide by potentiometry is in agreement with those obtained by conductometric titrations and the results have been discussed in this paper.

EXPERIMENTAL

Analar (B.D.H.) reagents were used. Uranium in the solution of uranyl nitrate was estimated as U_3O_8 as described in part I (*loc. cit.*). The solution of potassium ferrocyanide was estimated by titrating against a standard solution of potassium permanganate.

In all the titrations potassium ferrocyanide containing 1% potassium ferricyanide was used (Kolthoff, Kolthoff and Furman, "Potentiometric Titrations"). Platinum was used as an indifferent electrode (Muller, *Z. physikal. Chem.*, 1914, **88**, 44) which was used in conjunction with the saturated calomel electrode.

Ferri-ferrocyanide solution was dropped gradually from the burette into the solution of uranyl nitrate and the fall in E.M.F. was measured after each addition. Graphs were plotted between E(obs.) against the volume of ferrocyanide added. The equivalence point was found out from the steep fall in the potential indicated by the titration curves.

FIG. 1
A/1+A/10-$UO_2(NO_3)_2$

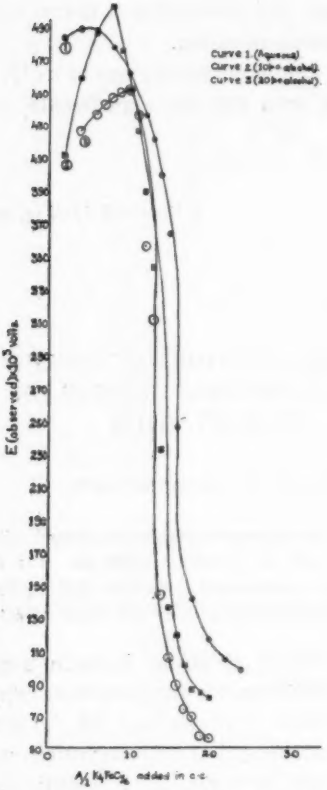
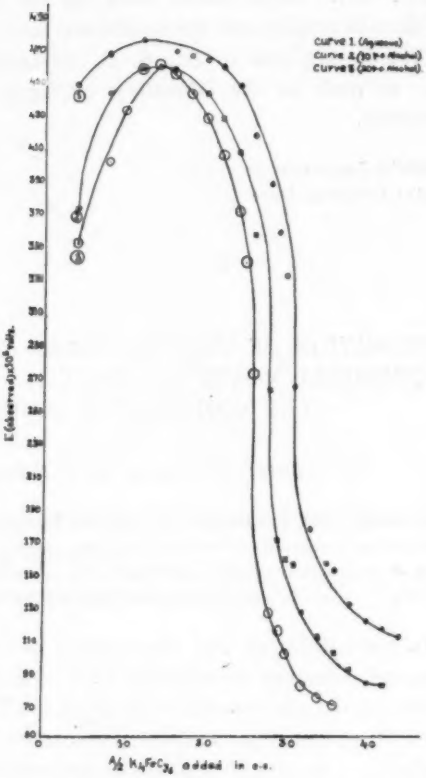


FIG. 2
A/2-K_4FeCy_6 added to A/10-$UO_2(NO_3)_2$



The volume corresponding to the maximum fall was taken as the point of equivalence. Titrations were done in the presence of alcohol up to 20% by volume. $M/4.855$ solution of K_4FeCy_6 would be referred as A/1 solution and $M/4.912$ solution of $UO_2(NO_3)_2$ as A/1 uranyl nitrate solution.

TABLE I

	A/10-$UO_2(NO_3)_2$ soln. = 20 c.c. Alcohol = nil. (Fig. 1, curve 1).						
A/1-K_4FeCy_6 added (c.c.).	0.2	0.6	1.0	1.3	1.6	2.0	2.4
E(obs.) (volt)	0.482	0.486	0,460	0.420	0.245	0.115	0.097
	A/10-$UO_2(NO_3)_2$ soln. = 18 c.c. Alcohol = 2 c.c. (Fig. 1, curve 2).						
A/1-K_4FeCy_6 added (c.c.).	0.2	0.6	0.9	1.2	1.5	1.7	2.0
E(obs.) (volt)	0.410	0.485	0.474	0.388	0.135	0.100	0.080
	A/10-$UO_2(NO_3)_2$ soln. = 16 c.c. Alcohol = 4 c.c. (Fig. 1, curve 3)						
A/1-K_4FeCy_6 added (c.c.).	0.4	0.8	1.1	1.4	1.7	2.0	
E(obs.) (volt)	0.425	0.446	0.435	0.143	0.073	0.056	

TABLE II

A/10-UO_2 soln. = 20 c.c. Alcohol = nil. (Fig. 2, curve 1).

A/2-K_4FeCy_6 added (c.c.)	0.4	1.6	2.2	2.8	3.0	3.5	4.0	4.4
E(obs.) (volt)	0.445	0.466	0.456	0.385	0.330	0.155	0.120	0.110

A/10-$UO_2(NO_3)_2$ soln. = 18 c.c. Alcohol = 2 c.c. (Fig. 2, curve 2).

A/2-K_4FeCy_6 added (c.c.)	0.4	1.6	2.4	3.0	3.4	4.2
E(obs.) (volt)	0.370	0.455	0.404	0.157	0.110	0.081

A/10-$UO_2(NO_3)_2$ soln. = 16 c.c. Alcohol = 4 c.c. (Fig. 2, curve 3).

A/2-K_4FeCy_6 added (c.c.)	0.4	1.2	1.8	2.4	2.8	3.2	3.6
E(obs.) (volt)	0.349	0.455	0.440	0.369	0.125	0.080	0.069

TABLE III

Tabulation of the results of the potentiometric titrations of uranyl ferrocyanide.

Theoretical value : 9.88 c.c. of $M/4.855$ $K_4FeCy_6 \equiv$ 10 c.c. of $M/4.912UO_2(NO_3)_2$.

A/10-$UO_2(NO_3)_2$ in the beaker (v c.c.).	Alcohol added.	K_4FeCy_6 required for v c.c. of A/10-uranyl nitrate (v_1).	K_4FeCy_6 calculated for 20 c.c. of A/10-uranyl nitrate [(v_1/v)20].	Equiv. vol. of A/10-K_4FeCy_6 [n(v_1/v)20].	Compound.	Curve.
A/1-K_4FeCy_6 added to A/10-$UO_2(NO_3)_2$. Conc. ratio (n) = 10 : 1.						
20 c.c.	0 c.c	1.60 c.c.	1.60 c.c.	16.0 c.c.	$K_2(UO_2)FeCy_6$, $0.235UO_2(NO_3)_2$	1
18	2	1.48	1.64	16.4	$K_2(UO_2)FeCy_6$, $0.20UO_2(NO_3)_2$	2
16	4	1.32	1.65	16.5	$K_2(UO_2)FeCy_6$, $0.197UO_2(NO_3)_2$	3
A/2-K_4FeCy_6 added to A/10-$UO_2(NO_3)_2$. Conc. ratio (n) = 5 : 1.						
20	0	3.10	3.1	15.50	$K_2(UO_2)FeCy_6$, $0.274UO_2(NO_3)_2$	1
18	2	2.8	3.11	15.55	$K_2(UO_2)FeCy_6$, $0.270UO_2(NO_3)_2$	2
16	4	2.6	3.25	16.25	$K_2(UO_2)FeCy_6$, $0.216UO_2(NO_3)_2$	3

DISCUSSION

The summary of results (Table III) suggests the formation of the compound of the type $K_2(UO_2)FeCy_6$, $xUO_2(NO_3)_2$. The value of x decreases with the concentration of alcohol mixed with uranyl nitrate. The variation of the proportion of uranyl nitrate attached to the precipitated complex may be due to adsorption or hydrolysis of the precipitate or both. Since the potentiometric titration is carried out by adding ferrocyanide from the burette into uranyl nitrate taken in the beaker, the formation of adsorption complexes with uranyl nitrate is very probable. The other possibility of the formation

of molecular complex of the type $K_2(UO_2)FeCy_6$, $x\ UO_2(NO_3)_2$ may be expected from the hydrolysable character of uranyl ferrocyanide. In this case the quantity of potassium ferrocyanide required will be less than the equivalent amount as explained in the preceding paper (*loc. cit.*). The value of x in that case will be proportional to the degree of hydrolysis of uranyl ferrocyanide. It is, however, difficult to allocate the proportional contribution of adsorption and hydrolysis in modifying the composition of the adsorption complexes of uranyl ferrocyanide. Experimental work on hydrolysis and adsorption is in progress which may throw further light on the composition of such complex salts.

An interesting feature of the potentiometric titration curves of uranyl nitrate on potassium ferrocyanide is this that the potential at first rises, then falls rapidly. This rise is hardly observed in any other titration where oxidation-reduction electrode has been used.

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A NOTE ON INORGANIC CHROMATOGRAPHIC ESTIMATIONS FROM THE DIMENSIONS OF THE ZONE

By B. S. Srikantan and C. N. Venkatachallum

Srikantan and Krishnan (this *Journal*, 1949, **28**, 415) have used the chromatographic method of estimating copper in brass and bronze, and to measure the concentration from the dimensions of chromatograms have adopted Freundlich's adsorption isotherm. The data in the previous paper (*loc. cit.*) illustrate for copper cation from $M/25$ to $M/200$ strengths of nitrate solutions. The length of the chromatogram being directly proportionate to concentration, h/c was constant giving a value of 181 (av.) with 1 c.c. of the copper nitrate solution in each case and the diameter of the tube being 0.7 cm. and for the same composition but different diamater of tube in the same quantity of solution r^2h was constant.

The results in this paper with different quantities of solutions are shown in Table I.

Table I

Prepared alumina as before. 100-120 mesh. Strength of copper nitrate solution = $M/200$. Diameter of tube = 0.7 cm.

Quantity of solution.	Length of chromatogram.	Buffered to p_H 9.4
1 c.c.	0.4 cm.	0.3 cm.
2	1.1	0.6
3	2.6	1.0
4	3.1	—
5	3 7	—

It is seen from Table I, column 2 that the length of the chromatogram is not proportional to the quantity of the solution chromatographed. Thus, 5 c.c. of the solution of $M/200$ copper nitrate do not produce five times the length of the chromatogram of 1 c.c. of the same solution in the same tube. The length is more than five times. A similar observation has been made by us (unpublished) on the anionic chromatogram from phosphate solutions; while 1 c.c. of the phosphate solution gives 5 mm. of chromatogram (on alumina developed by ammonium molybdate) and 2 c.c. of the same solution give 12 mm. length.

It is perhaps most likely that as the solution to be chromatographed passes through the adsorbent, there is a change in the H-ion concentration at the surface of the adsorbent. Schawab *et al.* (*Naturwiss.*, 1934, **28**, 44; *Z. angew. Chem.*, 1937, **50**, 546, 691; 1938, **51**, 709) recommend for cations a p_H of 9.4 and for anions a p_H of 5.3. Alterations of p_H might affect the adsorbability of the ions under consideration and different volumes of solution passing through p_H range, optimum for the adsorption of ions, changes making the adsorption partially reversible and thus the column tends to

increase in length more than proportionately. Such a view looks very plausible in view of the work of Sacconii (*Gazzetta*, 1949, **79**, 141; *Nature*, 1949, **164**, 70) who has shown that acids and salts lower H -ion concentration of pure activated alumina. If pure alumina is held as a thick suspension in 0.1*N*-HCl the p_H is increased beyond 5.6, and with 0.2*M*-$CuSO_4$ and 0.2*M*-$NiCl_2$ the p_H of the former is changed from 3.45 and of the latter from 4.22 to a value as high as 5.8.

In the experiments described in this paper and the previous ones, the p_H of alumina was brought to 9.4 for cation adsorption by soaking it in water to which sufficient amminia was added to give the required p_H value. In view of the discussion above, the p_H 9.4 for alumina has now been obtained by a buffer solution, so that depletion of H-ions by cation adsorption may be balanced by the buffer. The buffer used for soaking alumina was made of 250 c.c. *M*/5-H_3BO_3 with 250 c.c. *M*/5-KCl + 185 c.c, *M*/5-NaOH, all made up to a litre. The data in column 3 of Table I for repetitions of these experiments under this condition, show the importance of buffering to correct p_H.

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BOILING POINTS OF MONOHALOGEN DERIVATIVES OF NORMAL PARAFFINS

By Yatendra Pal Varshni

Relationship between the boiling points of normal paraffins and their monohalogen derivatives has been studied. It has been found that the difference between the squares of the boiling points of a normal paraffin and its monohalogen derivative is a constant. The constant is different for different halogens.

In a previous communication (Varshni, this *Journal*, 1951, **28**, 535) a formula correlating the boiling points of the various members of the normal paraffins had been suggested.

A simple relationship has been found to exist between the boiling points of a normal paraffin and its monohalogen derivative, which can be represented by the formula:

$$T^2 - T_x^2 = K$$

where T and T_x are the boiling points (in degrees absolute at 1 atmos.) of the paraffin and the corresponding monohalogen derivative, and K is a constant. The results are recorded in Table I. The values of K for chloro, bromo and iodo derivatives are respectively 48900, 65330, 87720.

TABLE I

		Monochloro			Monobromo			Mono-iodo.		
Paraffin.	T.	T_x			T_x			T_x		
		(obs.)	(calc.)	Error.	(obs.)	(calc.)	Error	(obs.)	(calc.)	Error.
Methane	111.5	248.9	247.7	−1.2	276.56	278.86	+2.3	315.5	316.5	+1
Ethane	184.7	286.3	288	+1.7	311	315.3	+4.3	345.2	349	+3.8
Propane	230.9	319.7	319.7	0	343.9	344.3	+0.4	375.4	375.5	+0.1
Butane	272.6	351.1	351	−0.1	374.6	373.7	−0.9	404	402.5	−1.5
Pentane	309.1	380.3	380.1	−0.2	402	401.1	−0.9	429	428.2	−0.8
Hexane	342	407.1	407.3	+0.2	429	427.1	−0.9	453	452.4	−0.6
Heptane	371.5	432.6	432.4	−0.2	451.8	450.9	−1.9	475.95	475.05	−0.9
Octane	397.6	456.1	456	−0.1	474	473.7	−0.3	Decomposes		

The difference between the calculated and observed values of T_x does not exceed 1.5 % in any case. In most cases it is well below 1 %.

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